

Université de Montréal

**Modification des membranes échangeuses de cations
par polymérisation chimique de l'aniline**

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Université de Montréal
Faculté des études supérieures

Cette thèse intitulée:

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par polymérisation chimique de l'aniline**

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Sophie Tan

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Résumé

Les membranes échangeuses de cations sont utilisées pour de nombreuses applications électrochimiques, notamment les piles à combustible, les procédés d'électrolyse et l'électrodialyse. Or, certaines applications requièrent des membranes possédant une sélectivité particulière aux cations monovalents ou aux protons vis-à-vis des cations multivalents. Ainsi, l'objectif de ce projet fut d'améliorer la permselectivité des membranes échangeuses de cations commerciales (Neosepta CMX et Nafion) pour les protons en modifiant celles-ci par la polyaniline, un polymère chargé positivement.

Les études préliminaires ont d'abord démontré que la présence de la polyaniline (PANI) sur une membrane CMX, fabriquée à base de poly(styrène sulfonate) pouvait améliorer sa sélectivité pour les protons face aux ions Zn^{2+} et Cu^{2+} lors des électrodialyses en milieu acide en permettant d'obtenir un taux de fuite en cations bivalents inférieur à 0.5% par rapport à une valeur d'environ 10% pour la CMX non modifiée. Par la suite, la méthode de modification des membranes a été développée de façon à polymériser in situ l'aniline sur une seule face ou à l'intérieur de la membrane. Les paramètres de modification ont été étudiés dans le but d'obtenir la membrane composite possédant le meilleur comportement permselectif pour les protons vis-à-vis des cations bivalents. En utilisant des oxydants portant une charge négative ou une charge positive, il a été démontré qu'il était possible de contrôler le lieu de polymérisation de l'aniline au sein de la membrane CMX soit à la surface, avec $S_2O_8^{2-}$, ou uniquement à l'intérieur de la membrane, avec Fe^{3+} . Les membranes composites CMX-PANI ont été caractérisées par de nombreuses méthodes incluant la spectroscopie des photoélectrons-X (XPS), la microscopie électronique à balayage (SEM), les mesures de conductivité, l'électrodialyse et l'analyse thermogravimétrique (TGA). Les résultats montrent qu'il est nécessaire d'avoir une couche homogène,

mais pas nécessairement épaisse, de polyaniline à la surface de la membrane CMX pour obtenir un taux de fuite en Zn^{2+} très faible; une couche de PANI se trouvant uniquement à l'intérieur de la membrane CMX n'a aucun effet bloquant sur le transport des ions Zn^{2+} . Le blocage du transport des cations bivalents semble donc être principalement causé par une répulsion électrostatique de ces derniers. La possibilité d'utiliser une couche mince de PANI permet de maintenir la résistance ionique de la membrane composite dans un même ordre de grandeur que la membrane non-modifiée. Les membranes CMX-PANI semblent stables pour les électrodialyses de moins de 12 h et la couche de PANI ne semble pas se détacher de la membrane CMX, et ce, même après une quinzaine d'électrodialyses.

La formation des membranes composites Nafion-PANI a également été étudiée. Contrairement aux membranes CMX-PANI, il est beaucoup plus difficile d'obtenir une couche de PANI uniforme et mince à la surface ou à l'intérieur de la membrane. En fait, les données de SEM, microscopie à force atomique (AFM), XPS, spectroscopie infrarouge (FTIR), calorimétrie différentielle à balayage (DSC), TGA, conductivité et d'électrodialyse laissent croire qu'une grande partie de la polyaniline formée réside soit dans la phase ionique de la Nafion ou dans la zone intermédiaire entre les phases hydrophobe et hydrophile, dépendamment des conditions de polymérisation choisies. Dans le premier cas, la présence de PANI dans les régions ioniques bloque à la fois le transport des ions Zn^{2+} et des H^+ . Dans le deuxième cas, une conductivité ionique acceptable est obtenue, mais le taux de fuite en Zn^{2+} n'est pas suffisamment réduit. Ainsi, la membrane Nafion-PANI, préparée selon les conditions expérimentales utilisées dans ce projet, est peu intéressante pour les applications en électrodialyse.

Mots clés: membrane échangeuse de cations, modification des membranes, poly(styrène sulfonate), perfluorosulfonate, Nafion, Neosepta CMX, polyaniline, caractérisation des membranes, permselectivité, électrodialyse.

Abstract

Cation exchange membranes allow selective transport of cations in the presence of anions. These membranes are widely used in electrochemical techniques such as fuel cells, electrolysis and electrodialysis processes. However, some of these techniques require good selectivity to monovalent cations against multivalent cations. Hence, the main objective of this project was to improve the permselectivity of commercial cation exchange membranes (Neosepta CMX and Nafion) by modification with polyaniline, a positively charged polymer.

Preliminary studies have shown that the presence of polyaniline (PANI) on the CMX membrane, a poly(styrene sulfonate) based membrane, could improve its selectivity for protons vs. Zn^{2+} and Cu^{2+} , during electrodialysis in acidic media, resulting in a metal leakage lower than 0.5% as compared to a value of around 10% for the unmodified CMX membrane. Subsequently, the modification method was developed to polymerize aniline in situ at the surface or inside the membrane. The modification parameters were studied in order to obtain the composite membrane which has the best permselectivity behavior towards protons vs. bivalent cations. With the use of oxidants bearing a negative or positive charge, it was demonstrated that it is possible to control the polymerization site in the CMX membrane either at the surface, with $\text{S}_2\text{O}_8^{2-}$, or solely inside the membrane with Fe^{3+} . The composite membranes were characterized using several techniques including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), conductivity measurements, electrodialysis, and thermogravimetric analysis (TGA). The data showed that a homogeneous surface PANI layer, which can be very thin, was necessary to obtain a very low metal leakage, but that a PANI layer found only inside the membrane does not have any blocking behavior towards Zn^{2+} . Hence, the blocking effect towards bivalent cations seems to be mainly caused by electrostatic

repulsion. No sieving effect was observed. The addition of a very thin PANI layer does not decrease significantly the membrane proton conductivity. The CMX-PANI membranes seem to be stable for electrodialeses of less than 12 h and the PANI layer does not seem to detach from the CMX membrane, even after fifteen electrodialeses.

The preparation of Nafion-PANI membranes was also studied. In opposition to CMX-PANI membranes, it was found that it is much more difficult to obtain a uniform and thin layer of PANI at the surface or inside the membrane. In fact, SEM, atomic force microscopy (AFM), XPS, infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), TGA, conductivity and electrodialesis data suggest that a large portion of the PANI formed is found either in the ionic phase of Nafion or in the intermediate zone between the hydrophobic and hydrophilic phases, depending on the polymerization conditions. In the first case, the presence of PANI in ionic regions blocks both the transport of Zn^{2+} and H^+ . In the second case, the ionic conductivity obtained for the Nafion-PANI composite membrane is acceptable, but the Zn^{2+} leakage is not sufficiently reduced. Therefore, the Nafion-PANI membrane, prepared under the experimental conditions used in this work, is less interesting for electrodialesis applications.

Keywords: cation exchange membrane, membrane modification, poly(styrene sulfonate), perfluorosulfonate, Nafion, Neosepta CMX, polyaniline, membrane characterization, permselectivity, electrodialesis.

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Liste des abréviations et symboles

ABRÉVIATIONS

| | |
|----------|---|
| AFM | Microscopie à force atomique ou "Atomic Force Microscopy" |
| ANI | Aniline |
| ATR | réflexion totale atténuée ou "Attenuated Total Reflectance" |
| CEM | Membrane échangeuse de cations ou "Cation Exchange Membrane" |
| CPS | Coups par seconde ou "Counts per second" (en XPS) |
| CV | Voltammétrie cyclique ou "Cyclic Voltammetry" |
| DMFC | Pile à combustible au méthanol direct ou "Direct Methanol Fuel Cell" |
| DSC | Calorimétrie différentielle à balayage ou "Differential Scanning Calorimetry" |
| DTG | Différentielle de la courbe de perte en masse (voir TG) |
| ED | Électrodialyse |
| FTIR-ATR | Spectroscopie infrarouge à transformée de Fourier par réflexion totale atténuée ou "Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance" |
| fwmh ou | |
| FWMH | Largeur à la mi-hauteur du pic ou "Full Width at Half-Maximum" |
| HQ/BQ | Hydroquinone/Benzoquinone |
| IEC | Capacité d'échange ionique ou "Ion Exchange Capacity" (mmol/g ou méq/g) |
| IR | Infrarouge |
| kCPS | Kilocoups par seconde ou "KiloCounts Per Second" (en XPS) |
| LNCA | Accessoire de refroidissement à l'azote liquide ou "Liquid Nitrogen Cooling Accessory" (pour le DSC) |
| MEA | Membrane échangeuse d'anions |

| | |
|----------------------|---|
| MEC | Membrane échangeuse de cations |
| $m\text{éq } SO_3^-$ | Milliéquivalents de groupements sulfonate |
| Naf | Nafion |
| PANI | Polyaniline |
| PEMFC | Pile à combustible à électrolyte polymère ou "Proton Exchange Membrane Fuel Cell" |
| PPy | Polypyrrole |
| PVC | Poly(chlorure de vinyle) ou "Poly(Vinyl Chloride)" |
| R.S.F. | Facteur de sensibilité relatif de l'élément en XPS ou "Relative Sensitivity Factor" |
| SEM | Microscopie électronique à balayage ou "Scanning Electron Microscopy" |
| TG | Perte en masse observée en TGA (wt %) |
| TGA | Analyse thermogravimétrique ou "Thermogravimetric Analysis" |
| UV-vis | Ultraviolet-visible |
| XPS | Spectroscopie des photoélectrons-X ou "X-Ray Photoelectron Spectroscopy" |

SYMBOLES

| | |
|---------|--|
| A | Surface de pic ou surface de la membrane ou surface de l'électrode |
| A' | Surface de pic corrigée par le facteur de sensibilité |
| A'_i | Surface de pic corrigée par le facteur de sensibilité pour l'élément i |
| at. % | Pourcentage atomique |
| C_o | Concentration de l'espèce électroactive en solution (mol/cm^3) |
| C_M | Concentration en métaux (mol/L) |
| C_i^S | Concentration de l'espèce i dans le compartiment cathodique au temps T^S (mol/L) |
| C_i^0 | Concentration initiale de i (mol/L) |
| D_o | Coefficient de diffusion de l'espèce électroactive (cm^2/s) |
| E | Potentiel (V) |

| | |
|-------------|---|
| E° | Potentiel standard de réduction |
| E_b | Énergie de liaison |
| E_c | Énergie cinétique |
| F | Constante de Faraday = 96485 C/mol |
| h | Constante de Planck = 6.626×10^{-34} J•s |
| i | Élément ou ion quelconque |
| i_p | Courant de pic (A) |
| j | Densité de courant (mA/cm ²) |
| J_i | Flux de l'espèce i (mol/cm ² •s) |
| l | Épaisseur de la membrane (cm) |
| M | Métal |
| n | Nombre d'électrons échangés |
| R | Constante des gaz parfaits = 8.3145 J/mol•K |
| R | Valeur de résistance (Ω ou Ωcm^2) |
| R_{soln} | Résistance de la solution (Ω) |
| R_{mem} | Résistance de la membrane (Ω ou Ωcm^2) |
| T | Température (°C ou K) |
| T^S | Temps d'électrodialyse (s) |
| T_g | Température de transition vitreuse (°C) |
| % v/v | Pourcentage volumique |
| V_{final} | Volume final de la solution (L) |
| V_c | Volume de la solution cathodique (L) |
| wt. % | Pourcentage massique |
| z_i | Valence de l'ion i |
| ΔE | Différence de potentiel (V) |
| ϕ | Fonction de travail (constante en XPS) |
| σ | Conductivité (S/cm) |
| v | Vitesse de balayage en CV (V/s) |
| ν | Nombre d'onde (m ⁻¹) |

À mes parents, Hocsun et Layhin

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Chapitre 1

*Introduction générale:
les membranes échangeuses de cations*

1.1. HISTORIQUE DES MEMBRANES ET GÉNÉRALITÉS

Le premier document relatant le phénomène de perméabilité des membranes remonte au 4^e siècle avant J.-C. lorsque Aristote décrit la possibilité d'obtenir de l'eau potable en filtrant l'eau de mer à travers un récipient fait de cire.¹ Cependant, les travaux d'Aristote n'ont pas été répétés pendant deux mille ans. Ce n'est qu'en 1688 que la science des membranes débuta avec la publication des travaux de la Hire sur la perméabilité des vessies de porc pour l'eau.² Par la suite, Nollet découvrit le phénomène de pervaporation en 1748 qui consista à séparer l'eau et l'éthanol par évaporation à travers ces membranes fabriquées avec des vessies de porc. Le terme osmose fut introduit en 1827 par Henri Dutrochet qui fit la découverte de la dialyse. En 1829, Thomas Graham fut le premier à étudier la diffusion et la séparation des gaz. Graham développa également la loi des gaz (1833) et introduisit les membranes fabriquées avec le caoutchouc.¹ Adolf Fick a pour sa part publié les premiers travaux sur la diffusion des liquides en 1855.³ Durant cette même période, en 1850, Thompson et Way observèrent pour la première fois le phénomène d'échange ionique.⁴ En 1887, van't Hoff publia ses travaux sur les principes de la pression osmotique et de la dynamique des solutions diluées qui lui valurent le premier prix Nobel de chimie décerné en 1901.^{3, 5} Un chercheur important dans la science membranaire, particulièrement dans la science des membranes ioniques, fut Frédérik Donnan. Ce dernier introduisit en 1911 le concept de l'équilibre des espèces ioniques présentes en solution et placées de part et d'autre de la membrane (équilibre de Donnan). C'est aussi durant ces années qu'il élaborait la théorie sur le potentiel de Donnan, démontrant qu'une différence de concentration (ou de l'activité) des électrolytes de chaque côté de la membrane induit une différence de potentiel. Donnan suggéra également que la présence de groupements ioniques fixes dans la matrice de la membrane empêche le transport des co-ions, des ions de même charge (principe d'exclusion de Donnan).^{3, 6} Les procédés membranaires apparurent au début des années 40 avec le développement de deux procédés complètement différents. Le premier procédé membranaire industriel a été réalisé dans le cadre du *Projet Manhattan*, projet visant le développement de la bombe atomique, et

consistait en un procédé permettant de séparer l'isotope ^{235}U des autres isotopes de l'uranium par diffusion des gaz.⁷ Le deuxième procédé fut l'hémodialyse, système utilisé pour traiter le sang des malades atteints d'insuffisance rénale. Ce système permet entre autres d'extraire l'urée, l'acide urique, la créatinine et autres déchets métaboliques dans le sang tout en maintenant les métabolites et électrolytes nécessaires au corps humain.⁸

De nos jours, il existe plusieurs types de membranes permettant de séparer des ions, molécules ou particules selon leur charge, leur affinité ou leur taille, sous la forme gazeuse, liquide ou solide. Ces différents types de membranes peuvent servir à une ou plusieurs méthodes de séparation incluant les procédés de pervaporation, micro- et ultrafiltration, osmose, dialyse et électrodialyse, etc.

1.2. LES MEMBRANES IONIQUES

Tout comme les résines échangeuses d'ions, les membranes échangeuses d'ions ont la propriété de permettre le transport sélectif d'ions de même charge, soit les cations ou les anions. Cette sélectivité est possible grâce à la présence de groupements chargés positivement (membranes sélectives aux anions) ou négativement (membranes sélectives aux cations). Ainsi, par répulsion électrostatique (principe d'exclusion de Donnan), le transport des contre-ions (de charge opposée aux groupements ioniques fixes de la membrane) est favorisé aux dépens des co-ions (possédant la même charge que le groupement fixe) (Figure 1.1). Par exemple, les membranes échangeuses d'ions possèdent des groupements ioniques fixés de façon covalente à la structure de la membrane, soit des espèces chargées positivement telles que des alkyle-ammonium ($-\text{NR}_3^+$, $\text{R} = \text{H}$ ou alkyle) ou des phosphonium ($-\text{PR}_3^+$), soit des espèces chargées négativement telles que des sulfonates ($-\text{SO}_3^-$), carboxylates ($-\text{COO}^-$) ou phosphonates ($-\text{PO}_3^{2-}$).^{8,9}

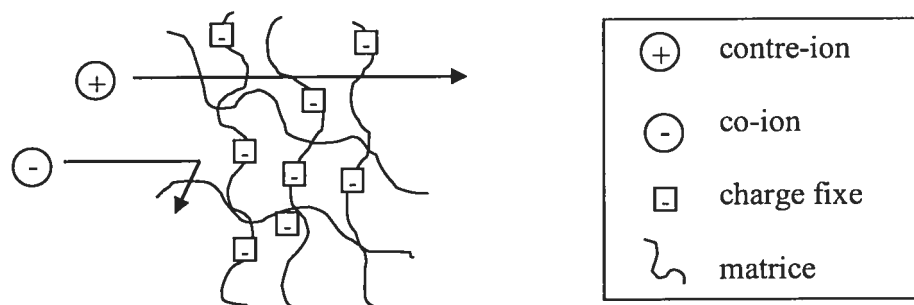


Figure 1.1. Représentation schématique des composantes d'une membrane ionique et du principe d'exclusion de Donnan.

Les membranes commerciales sont généralement fabriquées à base d'un polymère hydrophobe de type perfluoré ou de copolymères de styrène-divinylbenzène, le divinylbenzène servant d'agent de réticulation. La réticulation permet non seulement d'augmenter la stabilité chimique et thermique de la membrane, mais également de limiter le gonflement et la perméabilité à l'eau. En contrepartie, la réticulation augmente également la résistance ionique des membranes. Les structures de ces polymères, sous la forme de membranes échangeuses de cations (MEC), sont représentées à la Figure 1.2.^{8,9}

Les membranes à base de poly(styrène) sont généralement préparées par polymérisation du styrène et du 1,4-divinylbenzène dans un rapport variant entre 5:1 et 10:1 en présence d'un amorceur, tel que le peroxyde de benzoyle, à une température d'environ 80-100°C. Par la suite, les groupements sulfonates sont introduits par traitement du poly(styrène) à l'acide sulfurique (H_2SO_4) concentré à 70°C.⁸⁻¹⁰ Ces réactions sont présentées à la Figure 1.3.

Quant aux membranes perfluorées, il existe différentes stratégies de synthèse. En général, la synthèse du polymère est effectuée par polymérisation radicalaire entre le tétrafluoroéthylène ($CF_2=CF_2$) et un monomère substitué. Quelques exemples de réaction pour la formation du monomère sont donnés à la Figure 1.4. La polymérisation peut être réalisée en milieu aqueux ou non-aqueux.

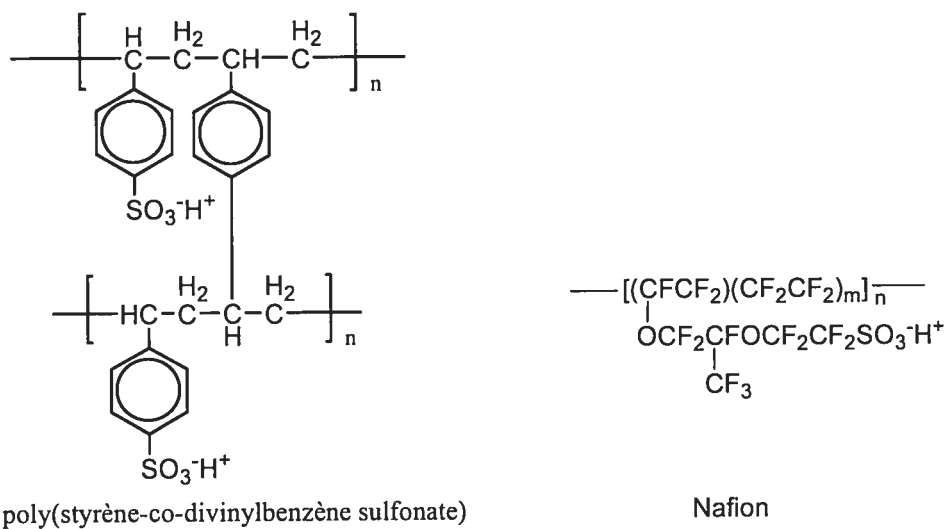


Figure 1.2. Structure générale des polymères utilisés dans la fabrication des membranes échangeuses de cations.

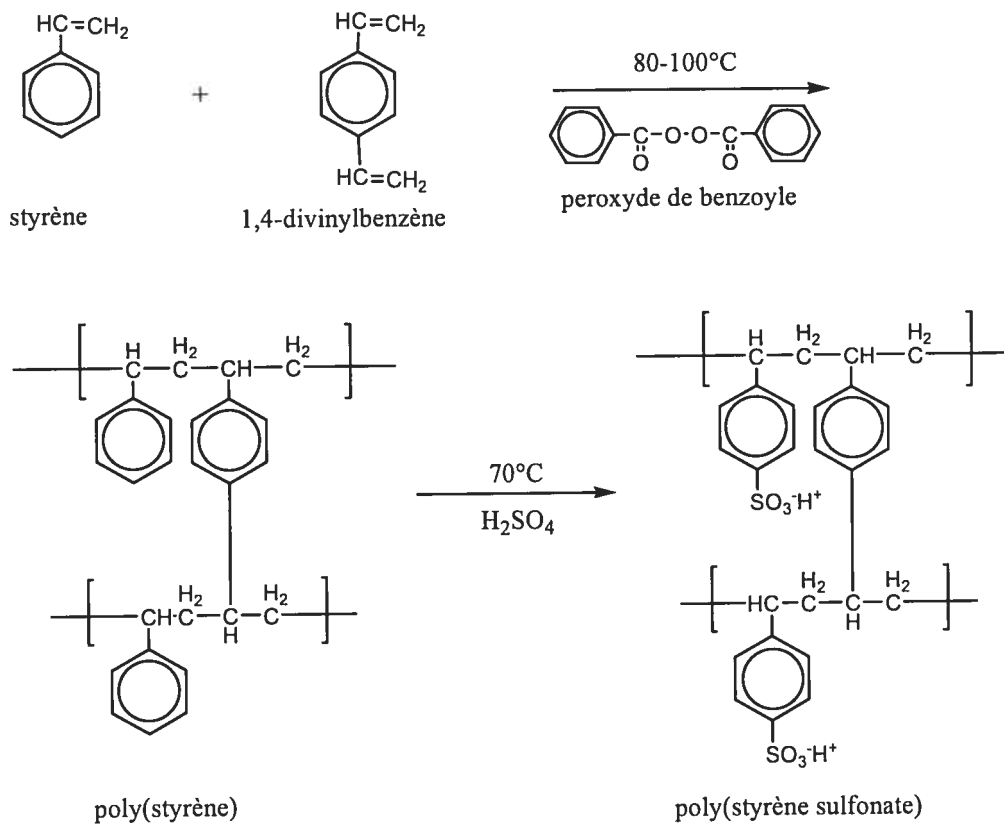
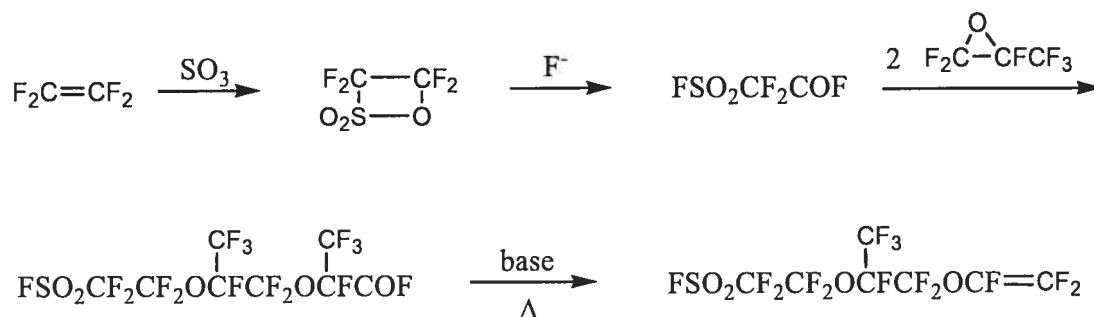


Figure 1.3. Synthèse des membranes ioniques à base de polystyrène.^{8,9}

Une fois le précurseur formé, il suffit soit d'introduire une diamine et quaterniser l'amine terminale pour former la membrane échangeuse d'anions ou d'hydrolyser la fonction $-\text{SO}_2\text{F}$ pour former la membrane échangeuse de cations. Dans ce dernier cas, un solvant halogéné inerte tel que le 1,1,2-trichloro-1,2,2-trifluoroéthane, le perfluorométhyle-cyclohexane, le hexafluorobenzène, ou le le perfluorooctane, est utilisé avec un amorceur de radicaux libres soluble tel que le N_2F_2 . En milieu aqueux, le polymère est synthétisé par émulsion ou suspension. Le monomère constitue la deuxième phase et l'amorceur est solubilisé soit dans la phase aqueuse pour la méthode par émulsion, ou dans le monomère pour la méthode par suspension. Un surfactant tel que le perfluorooctanoate est ajouté dans le milieu réactionnel. La dernière étape consiste à faire précipiter le polymère.

Exemple 1



Exemple 2

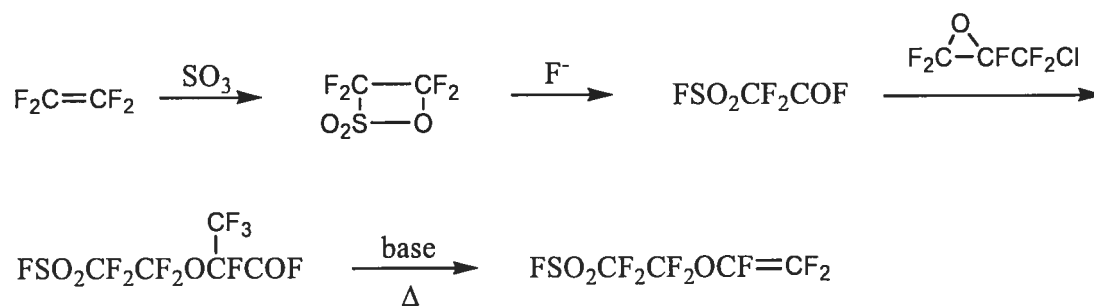
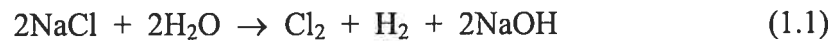


Figure 1.4. Synthèse des monomères substitués utilisés dans la fabrication des membranes ioniques perfluorées.⁹

1.3. LES APPLICATIONS DES MEC

Les membranes échangeuses d'ions ou plus spécifiquement, les membranes échangeuses de cations (MEC), sont utilisées dans de nombreuses applications électrochimiques. Entre autres, les MEC sont employées comme séparateur dans les cellules d'électrolyse à deux compartiments. En effet, ces membranes permettent soit de séparer les solutions entre les compartiments anodique et cathodique, sans quoi il y aurait une interférence entre les réactions anodiques et cathodiques; soit de déplacer un cation vers le compartiment cathodique. Un bon exemple de l'utilisation des MEC pour les électrolyses est le procédé industriel de la production du chlore (Cl_2) et de l'hydroxyde de sodium (NaOH). La Figure 1.5 montre comment la réaction suivante a lieu:



Dans ce cas, la MEC agit non seulement comme séparateur entre la réaction anodique



et la réaction cathodique



mais également comme transporteur d'ions Na^+ du compartiment anodique au compartiment cathodique favorisant ainsi la formation de NaOH en l'absence d'ions Cl^- .⁹

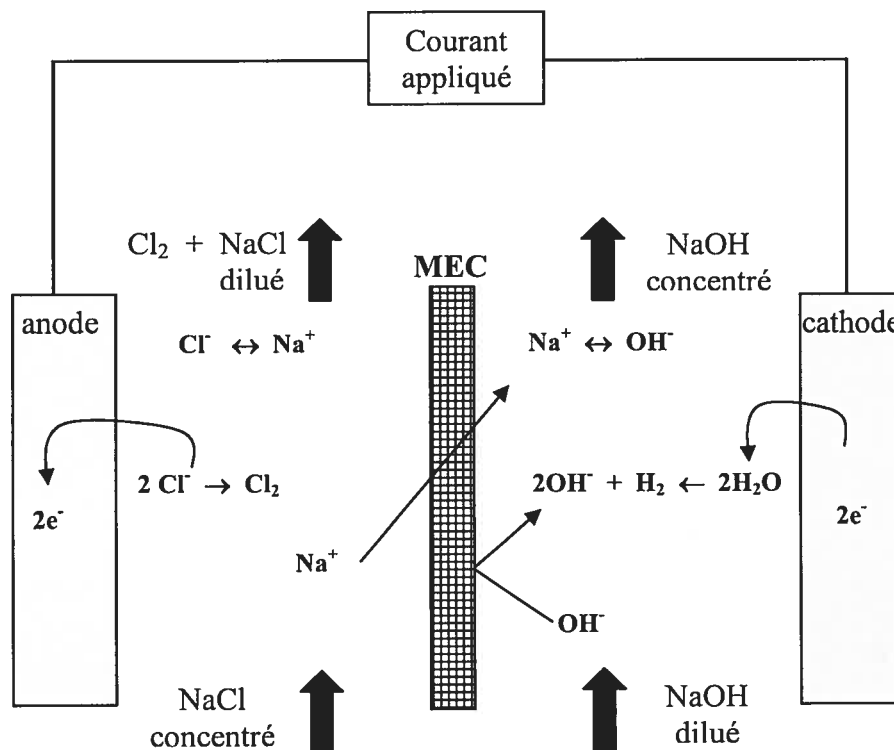


Figure 1.5. Utilisation d'une MEC dans la production du Cl_2 et NaOH par électrolyse. [Figure adaptée de la référence 9].

Une seconde technologie électrochimique employant les MEC et faisant présentement l'objet de nombreux travaux de recherche et de développement est la pile à combustible. Cette dernière est considérée comme une nouvelle technologie permettant de convertir l'énergie provenant de combustibles peu polluants tout en rejetant uniquement de l'eau et du dioxyde de carbone. Les applications potentielles de ces piles à combustible sont nombreuses et incluent notamment la navette spatiale, la voiture électrique, les ordinateurs et téléphones portatifs. Il existe plusieurs types de piles à combustible mais deux d'entre elles nécessitent l'utilisation d'une MEC: la pile à combustible au méthanol direct (Direct Methanol Fuel Cell - DMFC) et la pile à électrolyte polymère (Proton Exchange Membrane Fuel Cell - PEMFC).¹¹ Le principe de fonctionnement est le même pour ces deux piles et seul le combustible diffère d'une pile à l'autre. Les PEMFC nécessite l'utilisation de l'hydrogène pur (H_2)

alors que les DMFC requièrent du méthanol (CH_3OH), un carburant plus dense, plus facile à entreposer et à transporter. La Figure 1.6 illustre, de manière simplifiée, les diverses composantes d'une pile ainsi que le rôle de chacune de ces composantes. Il s'agit d'un système comportant une anode à laquelle l'hydrogène est oxydé pour former des protons et des électrons. Les protons sont transportés par un électrolyte polymère, en l'occurrence la MEC, au compartiment cathodique pour former de l'eau suite à une réduction de l'oxygène. Quant aux électrons, ils sont transportés dans un circuit électrique externe pour générer un courant électrique.

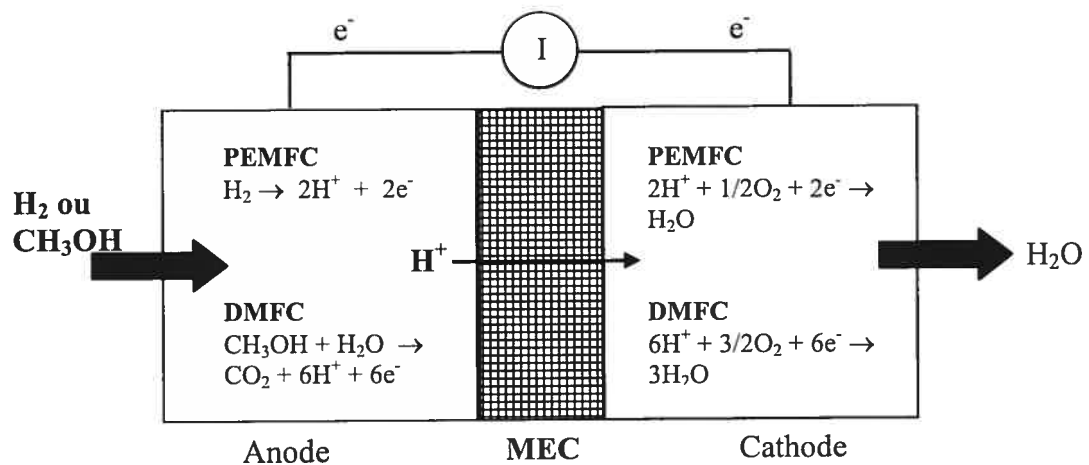


Figure 1.6. Représentation schématique simplifiée des composantes et du fonctionnement d'une pile à combustible de type DMFC et PEMFC.

Un troisième exemple de technologie électrochimique employant les MEC est l'électrodialyse, procédé faisant l'objet de cette thèse. Le système d'électrodialyse est composé d'une paire d'électrodes entre lesquelles sont placées plusieurs paires de membranes échangeuses d'anions (MEA) et échangeuses de cations (MEC). Sous l'effet d'un champ électrique, les anions se déplaceront vers l'anode et les cations vers la cathode tel qu'illustré à la Figure 1.7. La présence de membranes anioniques et cationiques disposées en alternance permet de concentrer certains ions dans des compartiments spécifiques. Ainsi, l'électrodialyse permet soit de réduire ou

d'augmenter la concentration d'un électrolyte. Contrairement aux procédés d'électrolyse, les réactions électrochimiques des électrodes ne sont pas directement impliquées dans le procédé d'électrodialyse. Les applications industrielles les plus communes de l'électrodialyse sont le dessalement de l'eau pour la rendre potable, l'extraction du sel provenant de l'eau de mer (utilisé au Japon) et la déminéralisation dans l'industrie agro-alimentaire et pharmaceutique. Une application également envisageable est la récupération des acides dans l'industrie minéralogique et métallurgique.¹² Cet exemple d'application est illustré à la Figure 1.7.

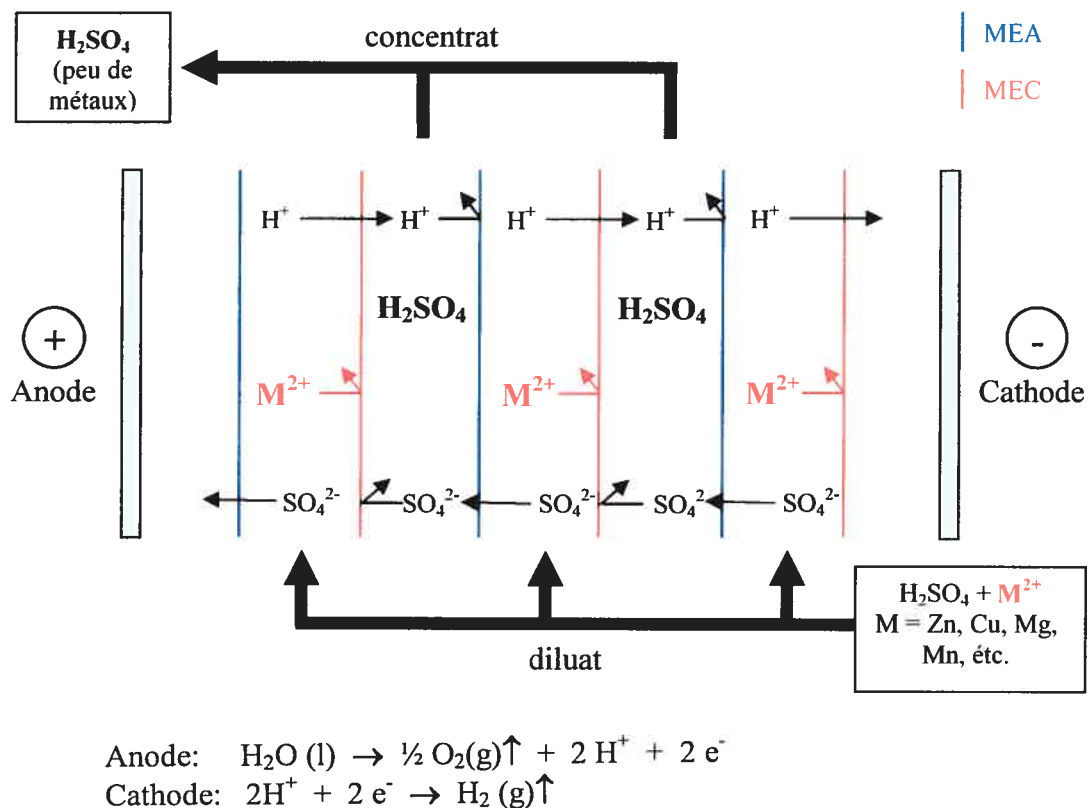


Figure 1.7. Représentation schématique d'un système d'électrodialyse employé pour la récupération des acides.

1.4. LA PROBLÉMATIQUE

Un obstacle majeur dans l'utilisation ou la commercialisation des procédés électromembranaires est le manque de sélectivité des membranes pour l'ion devant être transporté par la membrane, particulièrement dans le cas des membranes échangeuses de cations. En effet, les performances des procédés impliquant des membranes ioniques dépendent grandement des quatre propriétés principales suivantes: (i) la permselectivité, (ii) la conductivité ionique, (iii) la résistance mécanique et la stabilité dimensionnelle et (iv) la stabilité chimique et thermique.⁸

Dans un premier temps, les MEC doivent être perméables aux contre-ions tout en étant imperméables aux co-ions et au solvant, c'est-à-dire l'eau, dans la majorité des cas, ou le méthanol, pour les piles à combustible de type DMFC. Par ailleurs, la membrane la plus performante utilisée dans les DMFC jusqu'à présent est le Nafion[®], une membrane fabriquée à base de perfluorosulfonate (Figure 1.2).¹³⁻¹⁵ Cette membrane possède une bonne stabilité chimique et une bonne conductivité ionique. Par contre, la membrane Nafion présente aussi plusieurs désavantages dont celui de laisser traverser le méthanol et l'eau du compartiment anodique au compartiment cathodique. Le transport du méthanol engendre non seulement une perte de combustible, mais surtout, une diminution du rendement de la réaction de réduction à la cathode (Figure 1.6) par la contamination de cette dernière. De plus, le Nafion étant perméable à l'eau favorise le transport de cette dernière par effet d'entraînement accompagnant la migration des protons vers le compartiment cathodique, résultant ainsi en la déshydratation du compartiment anodique.

Pour certaines autres applications, les membranes échangeuses de cations doivent être permselectives à des cations monovalents. Par exemple, le système d'électrodialyse (Figure 1.7), utilisé pour la récupération des acides contaminés aux métaux, nécessite une bonne permselectivité des MEC aux protons et un bon blocage du transport des ions métalliques.^{12, 16} Ce système d'électrodialyse peut également être utilisé dans la purification des solutions de NaCl, contenant des ions Ca²⁺ et Mg²⁺, avant de les utiliser pour la production par électrolyse de NaOH et de Cl₂

(Figure 1.5).¹⁷ Encore une fois, ce dernier système requiert des MEC sélectives aux cations monovalents vis-à-vis des cations bivalents.

Dans un deuxième temps, la conductivité ionique doit sans aucun doute être la plus élevée possible puisque le rôle principal de la membrane est de transporter les ions d'un compartiment à l'autre. Une résistance ionique élevée entraînera une chute ohmique importante de la cellule et donc, une diminution de la performance de la cellule, que ce soit une cellule d'électrolyse, d'électrodialyse ou une pile à combustible. D'autre part, la stabilité mécanique de la membrane est essentielle pour envisager le développement de procédés industriels. La stabilité chimique de la membrane à des pH variant de 1 à 14 permet une utilisation plus variée de la membrane. Quant à la stabilité thermique, elle est nécessaire dans certaines applications nécessitant un fonctionnement à des températures élevées. Entre autres, dans l'exemple des piles à combustibles mentionné précédemment, l'utilisation de la membrane Nafion est limitée à 80°C, dû à la déshydratation de la membrane au-dessus de cette température, alors qu'il serait avantageux de faire fonctionner la pile à des températures plus élevées.

Malgré l'existence de nombreuses membranes ioniques sur le marché, très peu d'entre elles possèdent toutes les caractéristiques idéales. C'est pourquoi de nombreux travaux de recherche visent à développer de nouvelles membranes ioniques qui sont d'une part, davantage imperméables au méthanol tout en possédant une bonne conductivité des protons, une bonne stabilité chimique et thermique^{14, 15, 18-23} ou d'autre part, permselectives aux cations monovalents vis-à-vis des cations bivalents.^{17, 24}

1.5. AMÉLIORATION DE LA PERMSÉLECTIVITÉ DES MEC

Afin de résoudre les problèmes de sélectivité des membranes échangeuses de cations, deux approches sont généralement utilisées par les chercheurs: (i) la création de nouveaux polymères par voie de synthèse ou (ii) la modification des membranes déjà existantes sur le marché. Par exemple, dans le cas des piles à

combustibles, l'équipe de Savinell, Wainright et collaborateurs ont développé une nouvelle membrane à base de polybenzimidazole dopé à l'acide phosphorique (Figure 1.8) qui possède à la fois une bonne conductivité des protons, une bonne stabilité thermique et mécanique de même qu'une faible perméabilité au méthanol.²⁵⁻²⁷ D'autres membranes fabriquées à partir de poly(éther éther cétone),^{28, 29} polyimide³⁰ et polyphosphazène^{31, 32} semblent également être moins perméables au méthanol que le Nafion et posséder des bonnes propriétés conductrices. Les structures de ces polymères sont illustrées à la Figure 1.8. La deuxième approche utilisée par les chercheurs pour améliorer les propriétés des MEC pour les piles à combustible consiste à modifier les membranes existantes en incorporant un oxyde inorganique, tel que le SiO_2 ,³³ le TiO_2 ^{34, 35} ou le ZrO_2 ,³⁶ en traitant la surface des membranes par ablation laser³⁷ suivie d'une pulvérisation de palladium,³⁸ en incorporant un second polymère au sein de la membrane Nafion, tel que le polypyrrole^{19, 22, 23, 39} ou la polyaniline.⁴⁰

En ce qui concerne l'amélioration de la permselectivité des MEC pour les cations monovalents en présence de cations multivalents, ces deux mêmes approches sont également utilisées. Par exemple, l'équipe de Pourcelly a démontré que des membranes de polyimides sulfonés possèdent une permselectivité pour les protons vis-à-vis des métaux bivalents supérieure à celle de le Nafion.⁴¹ Les auteurs attribuent cette amélioration à une taille plus faible des agrégats ioniques formées par les groupements sulfonates lorsque comparée au Nafion. Or, ces agrégats ioniques forment des canaux par lesquels les protons ou cations sont transportés à travers la membrane.⁴²

D'autres chercheurs modifient les membranes déjà existantes pour améliorer la permselectivité de ces dernières pour les cations monovalents. Entre autres, Sata et ses collaborateurs¹⁷ ont modifié des membranes échangeuses de cations en introduisant un groupement chargé positivement à la surface de ces MEC. La présence de cette couche chargée positivement permettra à la fois de transporter les cations monovalents et de bloquer le transport des cations multivalents.

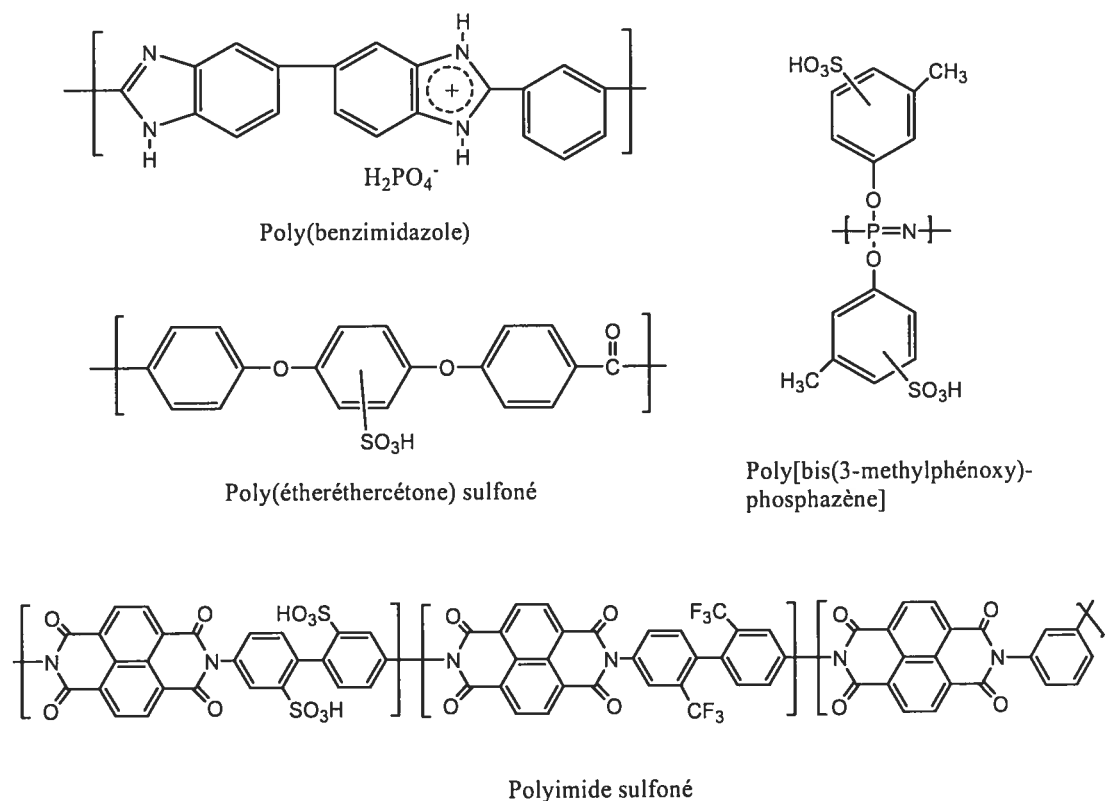


Figure 1.8. Exemples de polymères utilisés dans la fabrication des nouvelles membranes échangeuses de cations.

Par exemple, il est possible de greffer une diamine en formant une liaison sulfonamide entre les groupements sulfonates de la membrane et une amine.^{43, 44} Cette approche permet de former une couche de stable pendant une longue période d'électrodialyse. Par contre, la présence d'un groupement greffé sur le sulfonate (SO_3^-) augmente la résistance ionique des MEC en bloquant le site échangeur ionique. Une seconde méthode utilisée par l'équipe de Sata est de former un deuxième polymère chargé positivement à la surface de la MEC. Par exemple, des membranes de poly(styrène sulfonate) sur lesquelles une couche de poly(éthylène imine),⁴⁵ polypyrrole⁴⁶ ou de polyaniline⁴⁷ a été polymérisée à la surface démontrent une bonne permselectivité aux ions Na^+ face aux ions Ca^{2+} après électrodialyse en milieu neutre.

1.6. LES OBJECTIFS DU PROJET

Dans ce projet, nous tenterons de modifier par polymérisation chimique de l'aniline des membranes échangeuses de cations sulfonées, disponibles commercialement, dans le but d'améliorer leur perméabilité pour les protons face aux ions métalliques durant les électrodialyses en milieu acide.

Ainsi, l'objectif principal de cette thèse sera de caractériser les membranes composites poly(styrène sulfonate)/PANI et perfluorosulfonate/PANI dans le but de mieux comprendre les paramètres impliqués dans le transport perméable des protons en présence de cations multivalents et d'améliorer la perméabilité de ces membranes. Les objectifs spécifiques de ce projet seront:

- ◆ évaluer l'effet de la présence de la PANI polymérisée sur des membranes échangeuses de cations de type Neosepta[®] CMX
- ◆ étudier les paramètres de modification des membranes CMX et caractériser les membranes composites en fonction de ces paramètres de modification
- ◆ étudier la polymérisation de l'aniline sur des membranes de type Nafion[®] et comparer le comportement perméable de ces membranes composites aux membranes CMX/PANI
- ◆ étudier la stabilité des membranes composites les plus performantes obtenues dans le cadre de ce projet.

1.7. STRUCTURE DE LA THÈSE

La thèse sera divisée en huit chapitres, incluant celui-ci, dont quatre correspondent à des articles publiés ou soumis. Après avoir introduit les membranes ioniques, leur problématique et les objectifs de ce projet dans le chapitre 1, les principes de base des techniques de modification et de caractérisation des membranes utilisées dans ce projet seront présentés dans le chapitre 2. L'effet de la modification des membranes Neosepta[®] CMX par la polymérisation chimique de l'aniline sur les

propriétés de permselectivité des ions métalliques Zn^{2+} et Cu^{2+} et sur les propriétés physiques de la membrane sera démontré dans le chapitre 3. Ce dernier présente également les résultats de la première partie de l'étude des paramètres de modification (le temps d'échange des ions aniliniums). Une étude plus approfondie d'un second paramètre de modification (le temps d'oxydation de l'aniline) des membranes CMX est présentée au chapitre 4. Dans le chapitre 5, il sera démontré qu'il est possible de contrôler le site de polymérisation de l'aniline et que ce dernier aura un impact important sur la permselectivité de la membrane. Puisque la stabilité chimique et thermique des membranes composites est un facteur important dans le développement de nouvelles membranes permselectives, les résultats d'analyse thermogravimétrique, de stabilité suite aux électrodialyses répétées et de stabilité dans le milieu d'entreposage des membranes composites seront présentés dans le chapitre 6. Après avoir maîtrisé et mieux compris les conditions de modification des membranes fabriquées à base de poly(styrène-co-divinylbenzène sulfonate), les connaissances acquises seront utilisées pour modifier des membranes de type perfluorosulfonate (Nafion). Les membranes composites Nafion/PANI seront caractérisées et leur comportement permselectif sera comparé aux membranes poly(styrène-co-divinylbenzène sulfonate)/PANI dans le chapitre 7. Et finalement, la conclusion générale et des perspectives de travail seront présentées dans le chapitre 8. Il est à noter que les références sont données à la fin de chacun des chapitres.

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Chapitre 2

*Méthodes expérimentales:
les principes de base*

2.1. INTRODUCTION

Ce chapitre présente quelques détails expérimentaux non mentionnés dans les chapitres subséquents ainsi que certaines notions théoriques sur la polymérisation et les méthodes de caractérisation utilisées. Ces techniques de caractérisation sont divisées en trois catégories soit: les méthodes de caractérisation de surface, les méthodes électrochimiques et les méthodes thermiques. La majorité des détails expérimentaux ont été omis dans ce chapitre puisqu'ils seront présentés dans les chapitres subséquents.

2.2. MODIFICATION DES MEC PAR POLYMÉRISATION CHIMIQUE DE L'ANILINE

2.2.1. La polyaniline (PANI)

La polyaniline est un polymère qui possède des propriétés intéressantes au niveau de sa stabilité environnementale, c'est-à-dire non soluble dans l'eau et stable au contact de l'air, de ses propriétés rédox et de sa conductivité électronique. C'est pourquoi la PANI est un matériau convoité pour de nombreuses applications¹⁻³ dans les domaines des senseurs, de l'électronique, de l'optique et des sciences membranaires.⁴ Par ailleurs, la polyaniline est déjà utilisée dans la fabrication de films anti-statiques, de revêtements anti-corrosion, de semi-conducteurs pour les diodes électroluminescentes et autres composantes électroniques.

Tel qu'illustré à la Figure 2.1, la PANI possède des groupements amines et imines présents sous différentes proportions dépendamment de son état d'oxydation. Seule la forme émeraude, possède une conductivité suffisamment élevée pour être considérée comme un polymère conducteur. La polyaniline sous la forme émeraude et dopée-p, généralement par un acide, possède une conductivité électronique pouvant atteindre 10^2 S/cm, correspondant à la conductivité minimale

obtenue avec les métaux à la température de la pièce.^{5,6} La forme émeraude est également la forme la plus stable et la plus simple à synthétiser.

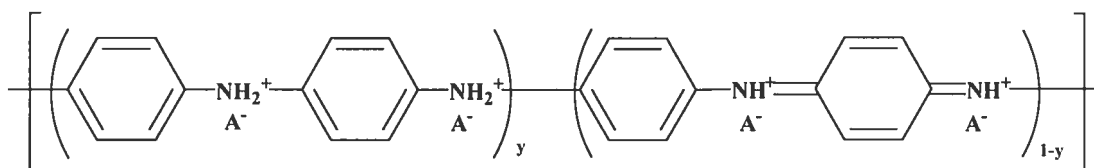


Figure 2.1. Structure des diverses formes de PANI: $y = 0$ correspond à la forme pernigraniline, $y \cong 0.5-0.7$, émeraude et $y = 1$, leucoémeraude. A^- représente le contre-ion dopant.

2.2.2. Synthèse de la polyaniline

La PANI et les composites polymères contenant de la PANI peuvent être synthétisées par voie électrochimique ou chimique.^{7,8} La méthode électrochimique implique l'utilisation d'une électrode (voir description complète d'une cellule électrochimique à trois électrodes à la section 2.4.4) sur laquelle un potentiel oxydatif, choisi dans la plage de stabilité de la PANI, est appliqué à l'aide d'un potentiostat/galvanostat. Le domaine de potentiel dans lequel la PANI est stable varie selon l'électrolyte choisi. Afin de préparer des composites polymère-PANI, il suffit de recouvrir l'électrode de travail avec un polymère non-conducteur, tel le Nafion, tremper l'électrode dans une solution d'aniline et appliquer un potentiel oxydatif.⁹ La polyaniline sera ainsi formée dans la matrice du polymère isolant. Cette technique est efficace mais elle est limitée par les dimensions de l'électrode utilisée et à des films composites relativement minces.

La méthode chimique est basée sur le même principe que la méthode électrochimique. Cependant, l'oxydation est effectuée à l'aide d'un oxydant chimique. Plusieurs oxydants, incluant le $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{K}_2\text{S}_2\text{O}_8$, H_2O_2 , FeCl_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , $\text{Ce}(\text{SO}_4)_2$, ont déjà été étudiés dans la synthèse de la PANI.¹⁰⁻¹² Certains de ces oxydants dont le $(\text{NH}_4)_2\text{S}_2\text{O}_8$ sont davantage utilisés dû à

l'absence d'atomes métalliques pouvant demeurer emprisonnés dans la matrice polymérique après polymérisation.

2.2.3. Méthode de modification des membranes

La modification est réalisée dans une cellule de Teflon[®] à deux compartiments illustrée à la Figure 2.2a. Cette cellule permet de modifier une seule face de la membrane sur une surface géométrique de 9.8 cm². La membrane est placée entre les deux compartiments de la cellule munis d'un joint torique assurant une bonne étanchéité de la cellule.

Avant la modification, les membranes sont conditionnées dans 1 M HCl pendant au moins 24 heures. Ensuite, les membranes sont modifiées soit par la méthode à deux étapes (chapitres 3 à 7) ou par la méthode à une étape (chapitre 5) (Figure 2.2b). Le compartiment contenant l'oxydant est toujours mis sous agitation durant la réaction. Une fois la modification complétée, la membrane est retirée de la cellule et rincée à l'eau nanopure avant d'être conservée dans une solution de 1 M HCl ou de 1 M H₂SO₄.

Il est à noter que l'identification des membranes varie d'un chapitre à l'autre, dépendamment des paramètres de modification étudiés. La notation utilisée est spécifiée dans les parties expérimentales de chacun des chapitres.

2.3. MÉTHODES DE CARACTÉRISATION DE SURFACE

2.3.1. Spectroscopie des photoélectrons-X (XPS)^{13,14}

La spectroscopie des photoélectrons-X permet d'effectuer une analyse qualitative et semi-quantitative de la surface des échantillons sur une épaisseur de l'ordre de 5 à 10 nm. Cette technique permet non seulement de déterminer les atomes présents à la surface des échantillons, mais également de définir leur état

La surface de l'échantillon est irradiée par une source de photons, dans ce cas-ci, un faisceau monochromatique de rayons-X, possédant une énergie $h\nu$ et provenant généralement d'une source d'aluminium (Al $K\alpha$, $h\nu = 1486.6$ eV) ou de magnésium (Mg $K\alpha$, $h\nu = 1253.6$ eV). Suite à cette irradiation, un électron de coeur est éjecté de son orbitale sous forme de photoélectron. L'énergie cinétique (E_c) du photoélectron éjecté est reliée à son énergie de liaison (E_b) selon l'équation suivante:

$$E_b = h\nu - E_c - \phi \quad (2.1)$$

où ϕ représente une fonction de travail, déterminée suite à une calibration de l'instrument. L'énergie de liaison dépend de l'environnement chimique de l'atome. Ainsi, un atome possédant un degré d'oxydation plus élevé aura une énergie de liaison plus grande que ce même atome à un degré d'oxydation inférieur. De façon similaire, un atome voisin d'un deuxième atome très électronégatif, possèdera un nuage électronique moins dense et donc, une énergie de liaison plus élevée. L'effet de ce phénomène est illustré sur le signal XPS du carbone (figure 2.4).

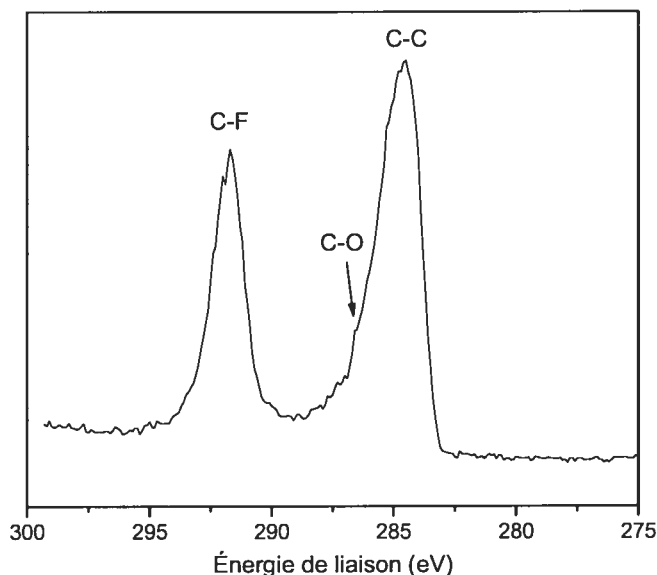


Figure 2.4. Exemple d'un spectre détaillé du C $1s$ illustrant l'énergie de liaison en fonction de son environnement chimique.

Il est important de noter que les échantillons analysés doivent être conducteurs électroniques. Dans le cas contraire, comme pour la majorité des polymères, il y aura une accumulation de charges positives à la surface des échantillons, ce qui affectera la résolution du pic et l'exactitude des valeurs d'énergie de liaison. Cette accumulation de charges positives est due à un appauvrissement des électrons de surface suite à une irradiation continue. Pour diminuer cet effet de charge, les échantillons analysés dans ce projet seront montés avec un anneau métallique conducteur électronique et l'analyse sera effectuée le plus près possible de l'anneau (Figure 2.5). À noter que l'anneau métallique déposé sur l'échantillon permet un contact électrique avec le support sur lequel est déposé l'échantillon. De plus, comme il sera mentionné dans la partie expérimentale des chapitres suivants, les valeurs d'énergie de liaison sont calibrées en fonction d'un élément majoritaire détecté à la surface d'un échantillon.

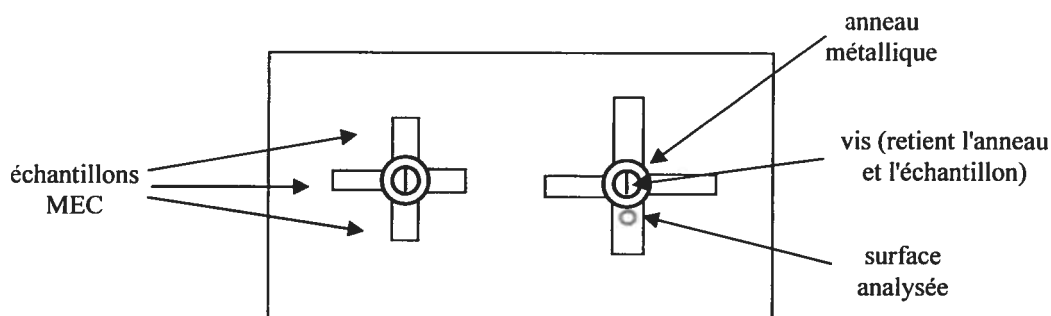


Figure 2.5. Schéma représentant un porte-échantillon utilisé en XPS sur lequel sont placées les MEC et la zone analysée.

Afin d'obtenir des résultats quantitatifs, la surface relative des pics est généralement utilisée. Cependant, la surface (A) des pics doit être divisée par le facteur de sensibilité relatif (R.S.F.) avant de pouvoir être utilisée dans les calculs:

$$A' = \frac{A}{R.S.F.} \quad (2.2)$$

où A' est la surface de pic corrigée. Les valeurs de R.S.F. seront données dans la partie expérimentale de chacun des chapitres contenant des résultats XPS. Les valeurs de A' permettent de calculer, entre autres, le % atomique d'un élément i quelconque à la surface de l'échantillon:

$$\% i = \frac{A'_i}{\Sigma A'_i} \times 100 \quad (2.3)$$

où $\Sigma A'_i$ est la somme des surfaces corrigées de tous les éléments présents à la surface.

2.3.2. Spectroscopie infrarouge à transformée de Fourier par réflexion totale atténuée (FTIR-ATR)^{13,15}

La spectroscopie infrarouge est une technique qualitative et quantitative généralement employée pour la détection de groupements fonctionnels ou d'hétéroatomes dans les composés organiques. L'infrarouge couvre la région spectrale entre 12800 et 10 cm^{-1} . Cette région peut être divisée en trois sections soit l'infrarouge proche, moyen et lointain. Cependant, la majorité des spectromètres infrarouges permettent l'acquisition des spectres dans la région de l'infrarouge moyen, c'est-à-dire entre 4000 et 400 cm^{-1} . C'est par ailleurs la région qui permet d'identifier la majorité des composés organiques. Le faisceau infrarouge incident correspond à la gamme d'énergie associée aux différents modes de vibrations des molécules dont les principaux sont les élongations symétrique et asymétrique, les vibrations de déformation angulaire.

Quant à la réflexion totale atténuée (ATR), elle consiste à utiliser un prisme de ZnSe permettant de réfléchir le faisceau incident sur la surface de l'échantillon à multiples reprises (Figure 2.6). La multiple réflexion du faisceau incident sur

l'échantillon permet d'obtenir un signal plus intense. La profondeur de pénétration du faisceau à la surface de l'échantillon est de l'ordre de quelques micromètres. L'accessoire ATR a été nécessaire dans le cadre de ce projet parce que les membranes composites étaient trop foncées et trop épaisses pour permettre une analyse par transmission, la méthode FTIR conventionnelle.

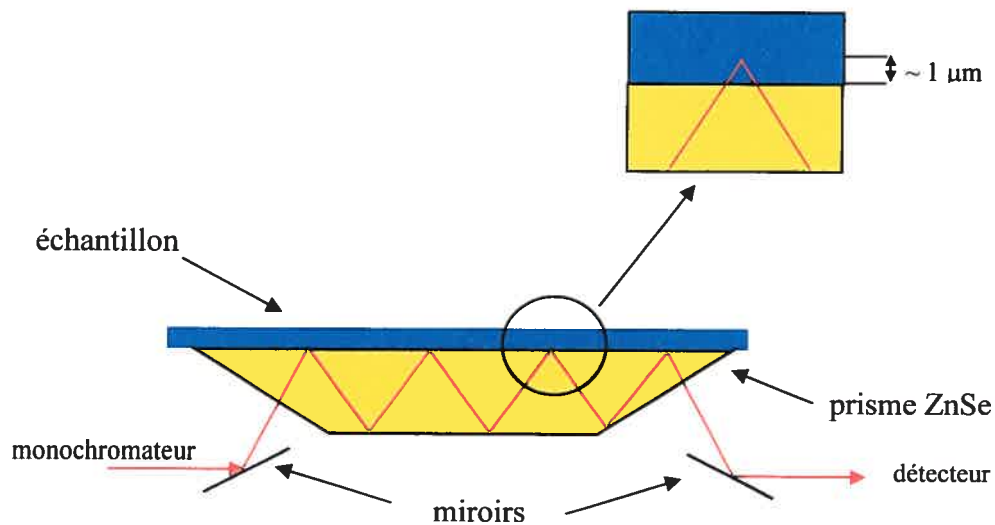


Figure 2.6. Illustration schématique du principe de l'ATR.

2.3.3. Microscopie électronique à balayage (SEM)

La microscopie électronique à balayage permet de fournir des renseignements au sujet de la morphologie et la composition chimique d'un échantillon solide. Le principe du SEM consiste à bombarder la surface de l'échantillon par un flux d'électrons primaires qui interagissent avec le solide afin de générer divers types d'émissions dont les principaux sont illustrés à la Figure 2.7.^{16,17}

En général, les électrons secondaires sont détectés afin d'obtenir une image topographique et morphologique (forme, dimensions, arrangements spatiaux,..) de la surface de l'échantillon alors que la détection des rayons-X permet d'obtenir la

composition chimique de la surface analysée. Dans certaines applications, il est également intéressant de détecter les signaux provenant des électrons rétro-diffusés, car ceux-ci donnent de l'information sur la densité des différentes phases présentes particulièrement pour les éléments ayant une masse atomique élevée.

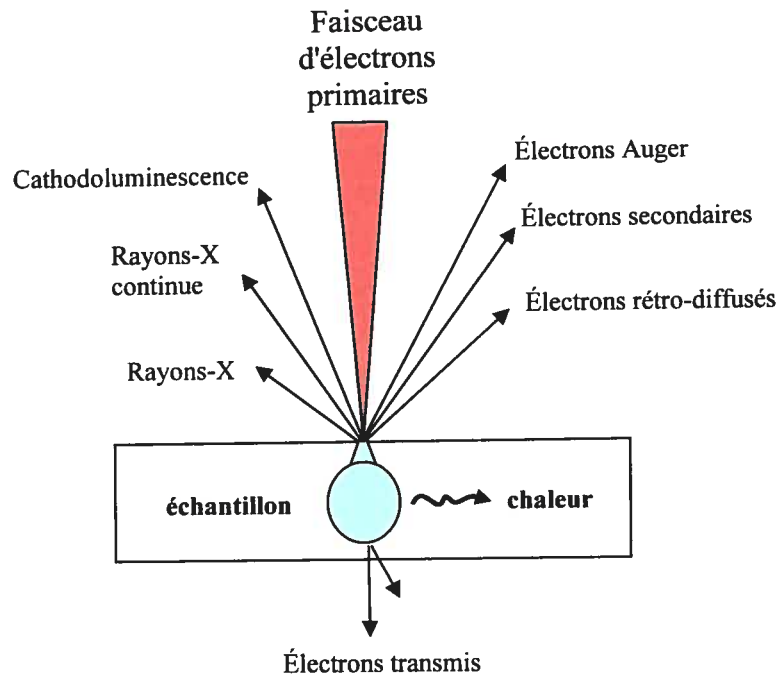


Figure 2.7. Différents types de rayonnement générés en microscopie électronique à balayage.

Par ailleurs, comme dans le cas des mesures XPS, il est préférable, en SEM, d'avoir des échantillons ayant une surface conductrice électronique. La présence d'une couche conductrice permet d'éviter une accumulation de charges à la surface pouvant déstabiliser l'image, affectant ainsi sa résolution, et même, dans le cas des polymères, permet d'éviter de brûler la surface trop rapidement. Une méthode communément utilisée en SEM pour rendre la surface des échantillons conductrice consiste à pulvériser une très fine couche d'or, de carbone ou de palladium sur le porte-échantillon.

2.3.4. Microscopie à force atomique (AFM)¹⁸

La microscopie à force atomique est une autre technique permettant d'imager la morphologie de surface. Cette technique, contrairement au SEM, possède l'avantage de pouvoir imager des échantillons non conducteurs à la pression et température ambiante ou même, d'imager en milieu aqueux évitant ainsi de modifier la morphologie des échantillons suite à la déshydratation. Le principe de l'AFM, illustré à la Figure 2.8, consiste à balayer la surface de l'échantillon avec un cantilevier sur lequel est placée une pointe faite de silicium, oxyde de silicium ou nitrure de silicium. Les forces d'interactions entre la pointe et la surface de l'échantillon font défléchir la pointe. Ces mouvements de la pointe sont suivis par un faisceau laser et un détecteur sensible aux mouvements du faisceau. Lorsque la force d'interaction entre la pointe et l'échantillon est maintenue constante, la pointe suit la topographie de l'échantillon. Le transducteur piézoélectrique permet de contrôler le déplacement de la pointe (ou de l'échantillon) en x , y et z .

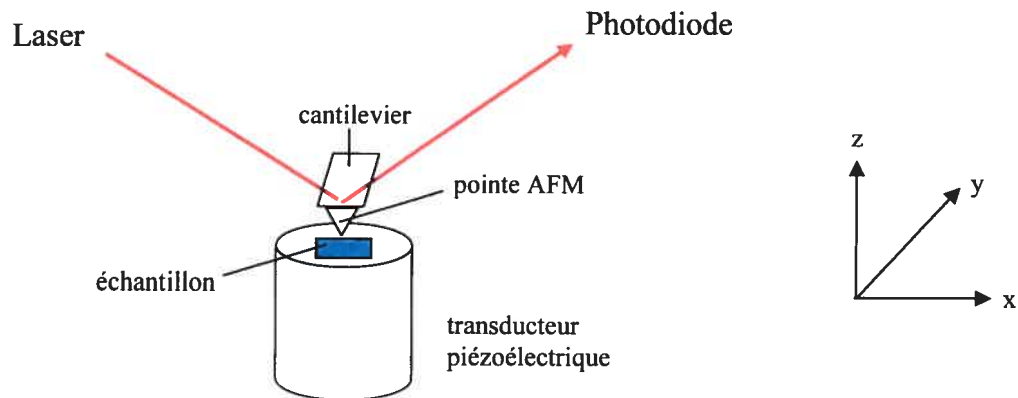


Figure 2.8. Principe de fonctionnement de l'AFM.

D'autre part, il est possible, en AFM, d'imager la surface d'un échantillon selon plusieurs modes incluant le mode contact et le mode intermittent. Le mode

contact est la méthode la plus simple où la pointe est en contact direct avec l'échantillon durant l'acquisition des images. Cependant, il présente certains désavantages particulièrement avec des échantillons biologiques ou des polymères puisque le balayage de la pointe sur ces surfaces "molles" peut déformer ces dernières dû aux forces latérales. Le mode intermittent, utilisé dans ce projet, consiste en faire osciller la pointe à une certaine fréquence et amplitude près de la surface. Ainsi, la pointe entre en contact avec l'échantillon pendant de courtes périodes de temps évitant ainsi d'endommager la surface.

2.4. MÉTHODES DE CARACTÉRISATION ÉLECTROCHIMIQUES

2.4.1. Électrodialyse

L'électrodialyse est une technique utilisée pour évaluer les propriétés de permselectivité des MEC et plus précisément dans le cadre de ce projet, d'évaluer le transport des cations bivalents à travers les MEC. La Figure 2.9 illustre la cellule de Teflon[®] à deux compartiments utilisée pour effectuer les mesures d'électrodialyse. La membrane étudiée est placée entre ces deux compartiments en plaçant la face modifiée de la MEC du côté anodique. Une solution acide contenant les métaux bivalents est placée dans le compartiment anodique et une solution contenant uniquement l'acide, du côté cathodique. Un courant est appliqué entre deux électrodes de platine forçant ainsi, par la présence d'un champ électrique, le transport des cations vers le compartiment cathodique. Il est à noter que dans ce système d'ED à deux compartiments, l'électroneutralité des charges est assurée par les espèces générées aux électrodes. La Figure 2.10 montre un exemple de courbe galvanostatique représentant la différence de potentiel entre les deux électrodes de platine en fonction du temps.

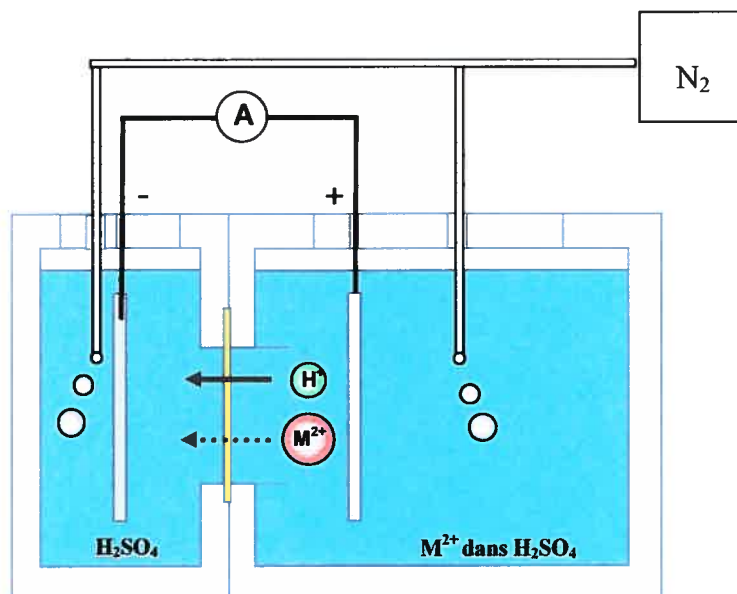
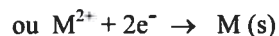
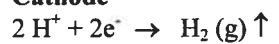
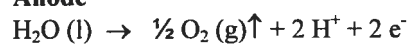
**Cathode****Anode**

Figure 2.9. Représentation schématique de la cellule utilisée pour les électroanalyses.

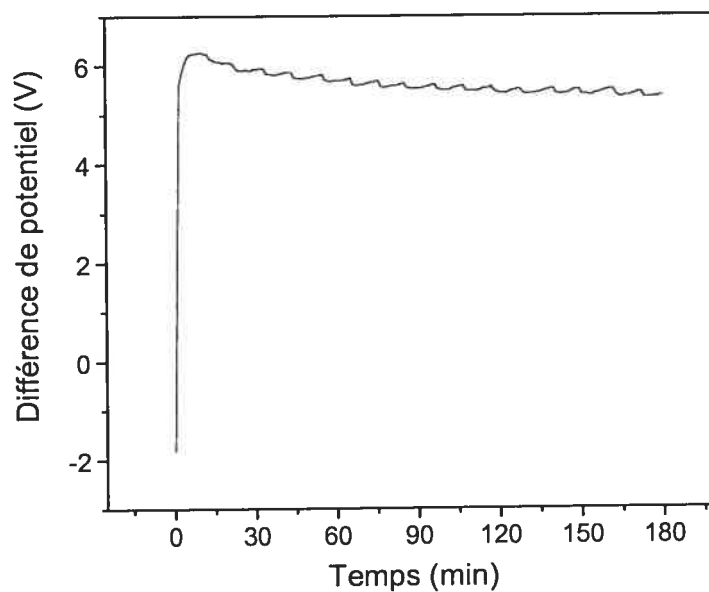


Figure 2.10. Exemple de courbe galvanostatique obtenue lors d'une électrolyse d'une solution de Zn^{2+} en milieu acide.

Suite à l'électrodialyse, les solutions anodique et cathodique sont analysées par absorption atomique afin d'évaluer la concentration d'ions métalliques. Ainsi, le taux de fuite en ions métalliques (% M) est calculé selon l'équation suivante:

$$\% M = \frac{mg M_{cathodique}}{mg M_{cathodique} + mg M_{anodique}} \quad (2.4)$$

où $mg M_{cathodique}$ et $mg M_{anodique}$ représentent la quantité de métaux en mg déterminée dans les compartiments cathodique et anodique, respectivement. La quantité de métaux est calculée à l'aide de la concentration des métaux, C_M (mg/mL), déterminée par absorption atomique et du volume final du compartiment, V_{final} (mL), après électrodialyse:

$$mg M = C_M \times V_{final} \quad (2.5)$$

Il est à remarquer qu'une cellule asymétrique a été employée simplement dans le but de concentrer davantage les métaux dans le compartiment cathodique.

2.4.2. Conductivité ionique

La conductivité ionique se distingue de la conductivité électronique par le fait que dans le premier cas, ce sont des ions qui transportent le courant alors que dans le deuxième cas, ce sont des électrons. Or, puisque les membranes échangeuses ioniques impliquent le transport d'ions, il est important d'évaluer la conductivité ionique des membranes. Cette méthode est complémentaire aux mesures d'électrodialyses et sert à caractériser les propriétés de permselectivité des membranes.

La Figure 2.11 illustre la cellule de Teflon[®] à deux compartiments utilisée pour les mesures de conductivité. Elle est constituée de deux paires d'électrodes: i) deux électrodes de platine entre lesquelles le courant est appliqué et ii) deux électrodes de références Ag/AgCl (KCl, 3 M) entre lesquelles la différence de

potentiel est mesurée en circuit ouvert. La distance entre la membrane et les électrodes de références doit être soigneusement ajustée. Il faut d'une part placer ces électrodes suffisamment loin de la surface de la membrane pour éviter les perturbations dues aux mouvements de convection pouvant être générées lorsqu'il y a un transport d'ions de part et d'autre de la membrane. D'autre part, il faut placer les électrodes de référence suffisamment près de la membrane pour permettre de détecter les changements en différence de potentiel causés directement par le transport ionique à travers la membrane et non par la solution ou par les réactions aux électrodes. En se basant sur les résultats obtenus par Krol¹⁹ et une étude préalablement effectuée dans notre laboratoire²⁰, nous avons choisi de placer chaque électrode de référence à 4 mm de la surface la membrane. Pour ajuster cette distance, un support à électrode a été monté sur la cellule et est contrôlé à l'aide d'une vis micrométrique. Un exemple de courbe de différence de potentiel en fonction du courant appliqué obtenue lors de ces mesures est illustré à la Figure 2.12.

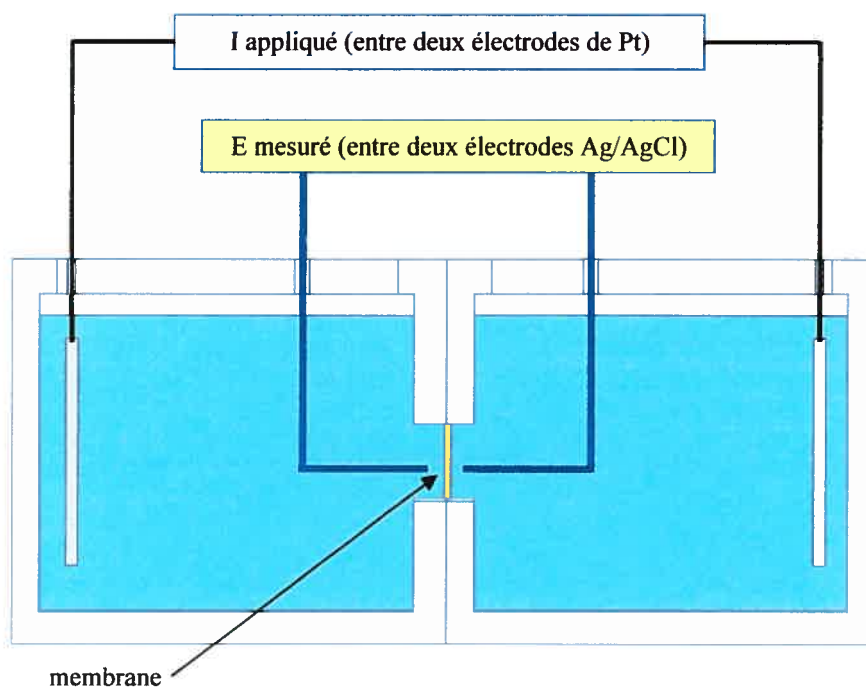


Figure 2.11. Représentation schématique de la cellule à deux compartiments utilisée pour les mesures de conductivité ionique.

Ainsi, selon la loi de Ohm:

$$E = RI \quad (2.6)$$

où E est la différence de potentiel lue entre les deux électrodes de référence (V), R , la résistance (Ω) et I , le courant appliqué (A), il est possible de déterminer la résistance ionique de la membrane. Or, la valeur R déterminée par l'équation 2.6 lors des mesures de conductivité représente la résistance totale de la cellule entre les deux électrodes de référence et peut être définie selon l'équation suivante:¹⁹

$$R = R_{soln} + R_{mem} \quad (2.7)$$

où R_{soln} est la résistance de la solution et R_{mem} , la résistance de la membrane. Par conséquent, la résistance de la solution doit être mesurée, avec la même cellule et dans les mêmes conditions expérimentales, pour ensuite la soustraire de la résistance totale mesurée en présence de la membrane pour obtenir R_{mem} . En connaissant la surface, A (cm^2), et l'épaisseur, l (cm) de la membrane, il est possible de calculer la conductivité ionique de la membrane, σ (Scm^{-1}):

$$\sigma = \frac{l}{R_{mem} \cdot A} \quad (2.8)$$

2.4.3. Capacité d'échange ionique

La capacité d'échange ionique (IEC) est définie comme étant le nombre d'équivalents de groupements ioniques par gramme de membrane sèche:

$$IEC = \frac{\text{még } SO_3^-}{\text{g membrane}} \quad (2.9)$$

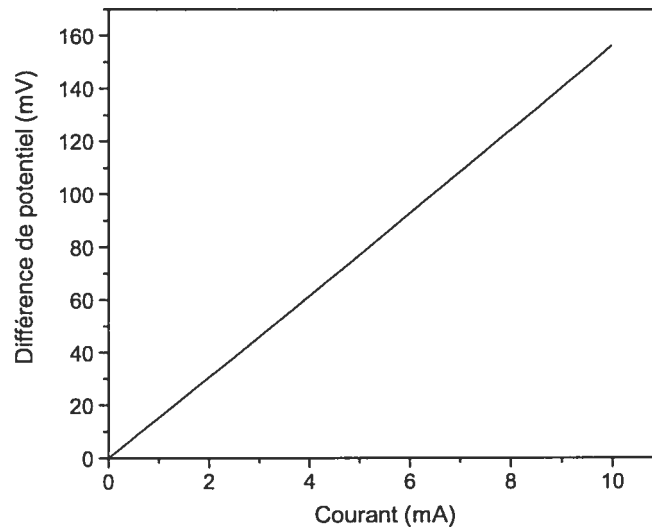


Figure 2.12. Exemple de courbe "courant-voltage" obtenue lors des mesures de conductivité en solution.

Cette valeur peut être déterminée par dosage des contre-ions dans la membrane. Typiquement, la mesure est effectuée par titrage des ions H^+ avec une base. Pour ce faire, les ions H^+ sont relargués en solution par échange ionique avec un second cation, Na^+ par exemple, et la quantité de protons relargués dans la solution de $NaCl$ est déterminée par titrage. Cependant, puisque dans ce projet, nous utilisons des membranes composites contenant à la fois des groupements sulfonates et amines, nous avons dû doser les ions Na^+ au lieu des ions H^+ . Le dosage des ions Na^+ est effectué par émission ou absorption atomique. Une représentation schématique du principe de la détermination des valeurs de IEC est donnée à la Figure 2.13. Pour assurer la validité de la méthode, des mesures de IEC avec les ions Na^+ sur les membranes composites commerciales non-modifiées ont été effectuées. Et effectivement, les valeurs obtenues par dosage du Na^+ sont équivalentes aux valeurs obtenues par dosage des H^+ . Par ailleurs, Palomo et Pintauro ont déjà démontré que la capacité d'échange ionique de la membrane Nafion est la même pour les ions Li^+ , Na^+ , Cs^+ , $(CH_3)_4N^+$ et $(CH_3CH_2)_4N^+$.²¹

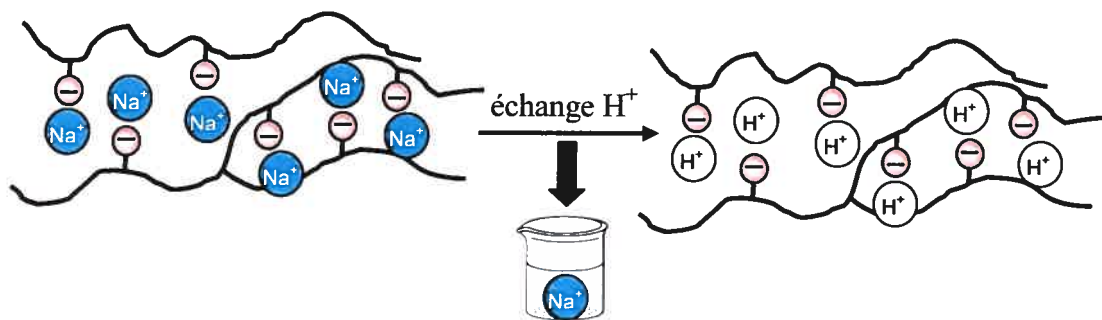


Figure 2.13. Représentation schématique de la détermination de la valeur de capacité d'échange ionique pour les MEC.

2.4.4. Voltammétrie cyclique

La voltammétrie cyclique est une technique couramment employée en électrochimie pour étudier les couples rédox, l'interface électrode/solution et la cinétique des réactions électrochimiques. La technique consiste à effectuer un balayage linéaire aller-retour en potentiel à une vitesse donnée (Figure 2.14a). Le potentiel est déterminé par rapport à une électrode de référence, en l'occurrence, une Ag/AgCl (3 M KCl). Les mesures sont effectuées dans une cellule à trois électrodes (Figure 2.14b) comportant une électrode de référence, un grillage de platine servant de contre-électrode et une électrode de travail. Dans ce projet, l'électrode de travail est un grillage d'acier inoxydable dans lequel est pressé un morceau de membrane.

Un voltammogramme typique d'un couple rédox réversible est illustré à la Figure 2.14c. En balayant le potentiel vers des valeurs positives, l'oxydation des espèces électroactives à la surface de l'électrode est observée par la présence d'un pic positif alors que leur réduction est observée dans le sens inverse.

Le courant de pic ainsi que sa surface sont proportionnels à la concentration d'espèces à la surface de l'électrode. Pour une réaction réversible, le courant de pic peut être défini selon l'équation suivante²²:

$$i_p = 0.4463 \left(\frac{F^3}{RT} \right)^{1/2} n^{3/2} A D_o^{1/2} C_o \nu^{1/2} \quad (2.10)$$

où i_p est le courant de pic (A), F , la constante de Faraday (96485 C/mol d'électrons), R , la constante des gaz parfaits (8.3145 J/mol•K), n , le nombre d'électrons impliquées dans la réaction, A , la surface de l'électrode (cm²), D_o , le coefficient de diffusion de l'espèce électroactive (cm²/s), C_o , la concentration de l'espèce électroactive en solution (mol/cm³) et v , la vitesse de balayage utilisée durant la mesure (V/s). De plus, en divisant la surface du pic (en A•V) par la vitesse de balayage (en V/s), il est possible de calculer la charge (en Coulombs) associée à la quantité d'espèces réduites ou oxydées.

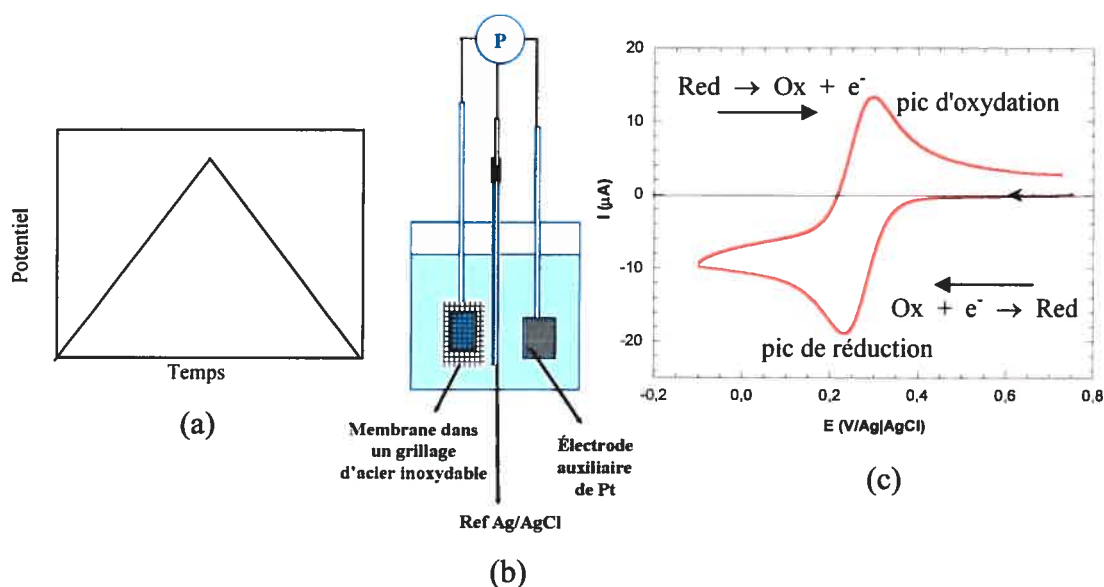


Figure 2.14. Principes de voltammétrie cyclique: (a) courbe illustrant la variation du potentiel en fonction du temps, (b) cellule utilisée pour les mesures et (c) exemple d'un voltammogramme.

La voltammétrie cyclique peut également être utilisée pour caractériser des polymères électroactifs déposés à la surface d'une électrode. Un polymère est électroactif ou conducteur lorsque la différence d'énergie entre la bande de valence et la bande de conduction est suffisamment faible, typiquement de l'ordre de 2 eV pour les polymères conducteurs, afin de permettre le transfert des électrons entre ces deux bandes. Ceci implique donc la présence d'électrons π dans la chaîne polymérique.

L'oxydation du polymère conducteur implique le transfert d'un électron de la bande de valence π à la bande de conduction, générant ainsi la formation d'un radical cation. La formation de cette charge positive est compensée par l'insertion d'anions, provenant de la solution, dans le polymère. Par opposition, la réduction mène à la formation d'un radical anion suite à l'ajout d'électrons dans la bande de conduction du polymère et la charge négative du polymère est compensée par l'insertion de cations. Ainsi, le dopage-p ou -n correspond à ces phénomènes d'insertion d'anions ou de cations, respectivement, faisant suite à la formation du radical chargé. Donc, le "dopant" est l'ion migrant vers la matrice polymère et sert à compenser la charge créée après oxydation ou réduction du polymère conducteur. Dans le cas de la polyaniline, il est possible d'observer, en voltammétrie cyclique, la présence d'un pic d'oxydation associé à un dopage-p (voir Section 4.4.2).

2.5. MÉTHODES DE CARACTÉRISATION THERMIQUE

2.5.1. Analyse thermogravimétrique (TGA)¹³

L'analyse thermogravimétrique consiste à mesurer de façon continue la perte en masse d'un échantillon en fonction de la température sous atmosphère contrôlée (azote, hélium, argon, air, oxygène ou autres gaz). Cette technique est généralement employée dans le but d'évaluer la stabilité thermique d'un polymère ou composé organique. Il est également possible de déterminer les proportions de matières organiques par rapport à un métal. En effet, dans la majorité des cas, les composés organiques sont complètement décomposés à la fin de l'analyse et seuls les oxydes métalliques sont retrouvés dans la cellule d'analyse.

L'instrument de TGA est composé principalement d'une balance thermique, d'une fournaise, d'un dispositif de purge à gaz et d'un ordinateur. La perte en masse est détectée par la déflexion d'un faisceau lumineux illuminant le bras de la balance par rapport à un deuxième bras agissant comme référence. Cette déflexion crée une différence de courant entre les deux photodiodes associées à chacun des bras. Ce

courant est amplifié et enregistré. Ce courant détecté passe également à travers une bobine placée entre deux aimants, générant ainsi un champ magnétique qui replace le bras à sa position initiale. Durant la mesure, l'échantillon et la référence sont placés dans une fournaise bien isolée permettant de contrôler la température. Il est généralement nécessaire de faire passer un gaz vecteur permettant de purger constamment la fournaise.

Un exemple de courbe thermogravimétrique (TG), c'est-à-dire de perte en masse en fonction de la température, est illustré à la Figure 2.15. La courbe en traits pointillés est la dérivée de la perte en masse (DTG) en fonction du temps. La courbe DTG met davantage en évidence les températures auxquelles les pertes de masses observées dans la courbe TG débutent et se terminent.

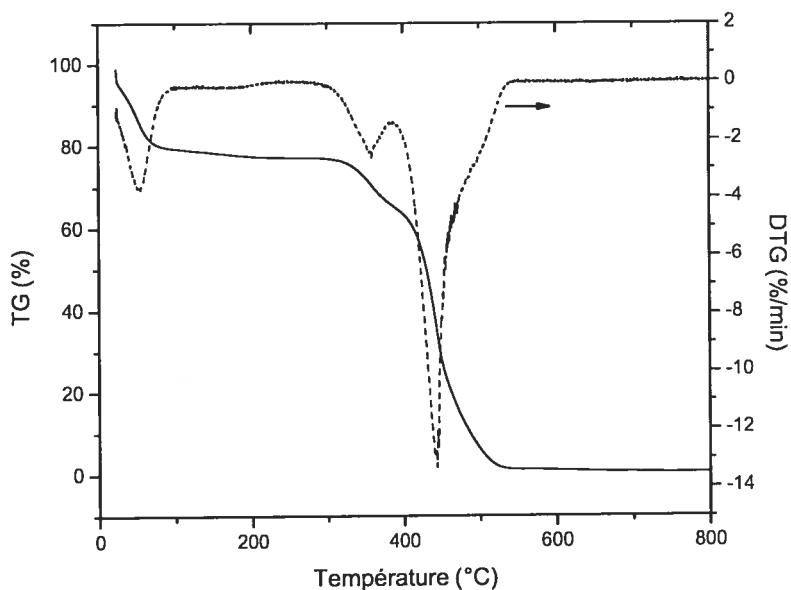


Figure 2.15. Exemple de courbes obtenues durant une analyse thermogravimétrique. La ligne en trait continu noir représente la perte en masse (TG) en % de l'échantillon et la ligne en traits pointillés bleus est la dérivée de la perte en masse en fonction du temps (DTG).

2.5.2. Calorimétrie différentielle à balayage (DSC)¹³

La calorimétrie différentielle à balayage ou DSC est une technique semblable à la TGA, mais qui étudie les transitions de phase d'un échantillon (un polymère, dans la plupart des cas) en fonction de la température. La transition vitreuse (T_g), la cristallisation et la fusion sont les transitions les plus couramment étudiées en DSC (Figure 2.16a). En général, la DSC est utilisée à des températures inférieures au début de la décomposition de l'échantillon. Il est préférable d'effectuer, au préalable, une mesure TGA de l'échantillon afin d'éviter d'atteindre la température de décomposition de cette dernière. Ainsi, on évite de contaminer inutilement la chambre d'analyse de l'instrument.

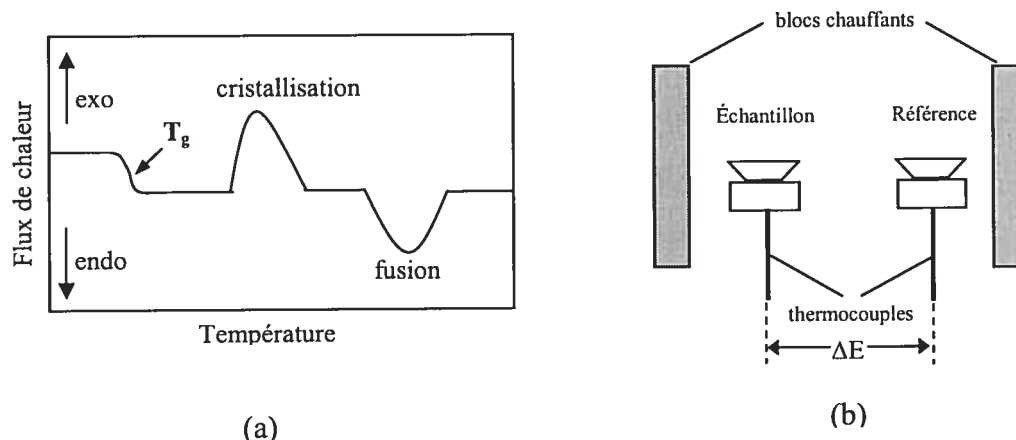


Figure 2.16. Illustration schématique des transitions de phase pouvant être observées en DSC (a) et des composants d'un appareil DSC (b).

Le principe, illustré à la Figure 2.16b, consiste à mesurer la différence de potentiel (ΔE) entre l'échantillon et une référence, qui consiste en une cellule vide de même type que celle utilisée pour l'échantillon, en fonction de la température. Cette différence de potentiel est amplifiée et convertie en température. Par la suite, l'appareil chauffera l'échantillon ou la référence de façon à maintenir la même température entre ces deux derniers. Ainsi, le flux de chaleur nécessaire pour

équilibrer la température entre les deux cellules est ce qui est le signal enregistré. Les mesures DSC sont effectuées sous atmosphère inerte (azote, hélium ou argon).

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Chapitre 3

Chemical Modification of a Sulfonated Membrane with a Cationic Polyaniline Layer to Improve its Permselectivity

Sophie Tan, Valérie Viau, Daphné Cugnod and Daniel Bélanger

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3.1. ABSTRACT

The surface of a cation-exchange membrane (NEOSEPTA) bearing sulfonate groups was modified by a thin polyaniline layer to produce a thin positively charged layer at its surface. This modification induces a slight modification of the surface morphology as evidenced by scanning electron microscopy and a decrease in ion exchange capacity. The presence of the polyaniline layer was confirmed by X-ray photoelectron spectroscopy. The selectivity of the modified and unmodified membranes towards protons versus metallic cations such as Zn^{2+} and Cu^{2+} were determined after electro dialysis in a two-compartment electrochemical cell. The data indicate that the transport of the metallic cations is decreased significantly following the modification of the membrane with the cationic polyaniline layer. The latter allows the transport of protons from the catholyte to the anolyte compartment with a much improved selectivity since the divalent cations are excluded from the membrane due to the electrostatic barrier created from the thin protonated polyaniline layer.

3.2. INTRODUCTION

Ion-exchange membranes make up a very important class of materials due to their various technological applications in electro dialysis, electrolysis and fuel cells. However, despite their widespread use in the aforementioned applications, these membranes often lack of selectivity or barrier properties which led to non-ideal performance. Thus, several approaches have been evaluated to improve the permselectivity of ion-exchange membranes.¹⁻⁹ In one of these approaches, Sata et al. demonstrated that the presence of a polypyrrole⁶ or polyaniline (PANI)⁷ layer at the surface of a commercial sulfonated cation-exchange membrane (CEM) (NEOSEPTA CM-1) improved the selectivity for specific ions transport. They have demonstrated the permselectivity of these composite membranes for Na^+ in the presence of Ca^{2+} ions for electro dialysis in neutral solutions.

Another area where permselectivity is crucial is for the recovery of acid from solutions containing metallic cations. In this case, the cation-exchange membranes should allow the transport of protons but block divalent cations such as Zn(II) and Cu(II). For this application, Sistat et al. have shown that a commercial CEM (Nafion) bearing a thin protonated polyethyleneimine film at the membrane surface demonstrated improved selectivity towards protons with respect to divalent cations, compared to a plain CEM.⁸ However, the long-term stability of these polymers and the resulting membranes were insufficient.

In this work, a Neosepta CMX membrane modified by a polycationic PANI layer is used in an acidic media in order to block the transport of multivalent heavy metal cations. This acidic pH favors the formation of a positively charged layer on the surface of the cation-exchange membrane caused by the protonic doping of PANI.¹⁰⁻¹⁶ We report herein the preliminary results of the characterization of these modified membranes using scanning electron microscopy and ion-exchange capacity measurements and their use in electrodialysis experiments in the presence of a sulfuric acid solution containing divalent zinc cations.

3.3. EXPERIMENTAL

3.3.1. Chemicals

Ammonium peroxodisulfate (EM Science), HCl (EM Science), NaCl (BDH), H₂SO₄ (EM Science) and ZnSO₄·7H₂O (Anachemia) were of A.C.S. reagent grade and used as received. Aniline (Aldrich) was distilled prior to use. Millipore water (18 MΩ·cm) was used for the preparation of all solutions.

3.3.2. Modification of Cation-Exchange Membranes

Before use, the Neosepta CMX membranes were conditioned in 0.5 M NaCl and 1 M HCl for more than 24 hours. The membrane modifications were performed

according to a method published by Sata et al. using a two-compartment cell containing the reagents in one compartment and water in the other, leading to a single-face modification.⁷ The protons of the commercial membrane was first ion-exchanged with the protonated aniline using a 10% aniline in 1 M HCl aqueous solution. After rinsing, the compartment was then filled with a 1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution to induce the polymerization. The polymerization time was 1 hour. The membranes were stored in 1 M HCl for more than 40 hours prior to characterization in order to ensure the protonation (or doping) of the PANI layer.

3.3.3. Ion-Exchange Capacity Measurements

All membranes were washed and stabilized several times in 1 M HCl, H_2O and 1 M NaCl alternatively for 1 hour in each solution. Then, the membranes were ion-exchanged with Na^+ by soaking them in a 1 M NaCl solution for 24 hours and in water for 30 minutes (to remove excess NaCl) and finally, they were dried at 65°C for 1 hour. After weighing the membranes, the Na^+ ions were ion-exchanged during 24 hours with H^+ using a 1 M HCl solution. The sodium concentration was determined by atomic emission spectroscopy.

3.3.4. Electrodialysis Experiments

Electrodialyses were performed in a two-compartment cell which contained 15 g Zn^{2+}/L in 0.5 M H_2SO_4 in the anodic compartment and 0.5 M H_2SO_4 in the cathodic compartment. The modified side of the membrane was placed facing the anolyte. A current density of $100 \text{ mA}/\text{cm}^2$ was applied during 3 hours using a M273 Potentiostat/Galvanostat (EG & G Princeton Applied Research). The content of both compartments were analysed by atomic absorption spectroscopy to determine their metal concentration.

3.4. RESULTS AND DISCUSSION

The chemical polymerization of aniline leads to the so-called doped and positively charged polyaniline.¹⁰⁻¹⁴ Following polymerization, polyaniline can also be reversibly doped and undoped by acid or alkaline treatments.¹⁰⁻¹⁴ In this work, the doped form of polyaniline is obtained by chemical polymerization on a single face of the membrane followed by an acidic treatment.

3.4.1. Scanning Electron Microscopy (SEM)

After polymerization, a green to dark purple layer, characteristic colors of PANI,^{7,16} appears on the modified face of the cation-exchange membrane. In order to characterize the properties of the adsorbed polyaniline, scanning electron microscopy photomicrographs were taken. The cross-sections of the unmodified CMX membrane and the modified membrane (CMX-PANI) are shown in Figure 3.1. Unfortunately, the polyaniline layer on the surface is not detectable, possibly because the deposited layer is too thin. Also, the fiber-type structure of polyaniline might not be very different from the structure of the base membrane. On the other hand, a contraction of the membrane thickness by approximately 10 μm is observed after modification. This could be attributed to the change in ionic interactions between the fixed ionic groups on the membrane and their counter ions suggesting that at least a portion of the polyaniline is present into the membrane and not only at its surface.

Figure 3.2 illustrates SEM micrographs of the membranes surfaces. A change in morphology is noticeable between the CMX and CMX-PANI membranes: a rougher surface is obtained after modification of the membrane. Hence, SEM images confirm that the polyaniline adsorbed is present both on the surface and in the membrane. These observations are in agreement with the ones published by Sata et al.⁷ Moreover, preliminary results obtained from our XPS studies demonstrate the presence of PANI on the surface of the CMX membrane and suggest that the layer formed is very thin (less than 50 \AA). This is indicated by the relative increase of the N $1s$ signal around 400 eV as well as the decrease of the S $2p$ component, at about

168 eV, of the sulfonate groups of the CMX membrane upon modification of the base membrane with polyaniline (Figure 3.3). The XPS results of the opposing face of the modified membrane corresponded to the spectra obtained for the unmodified CMX membrane indicating that PANI was not polymerized throughout the whole membrane. A detailed XPS study of polyaniline-modified CMX is currently underway in our laboratory and the results of this study will be reported elsewhere.

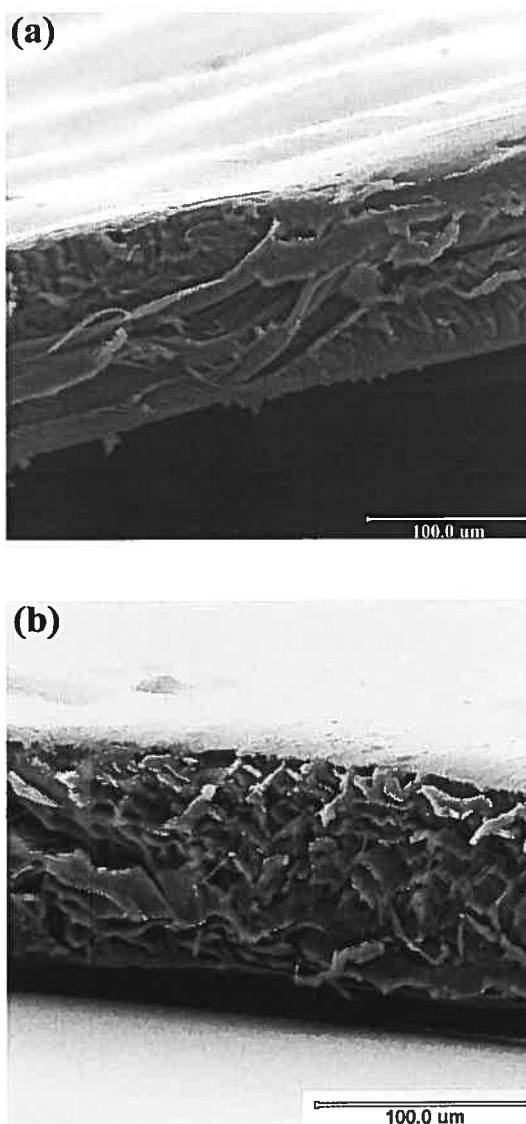


Figure 3.1. Scanning electron micrographs of the cross-section of the: (a) unmodified and (b) polyaniline modified CMX membranes.

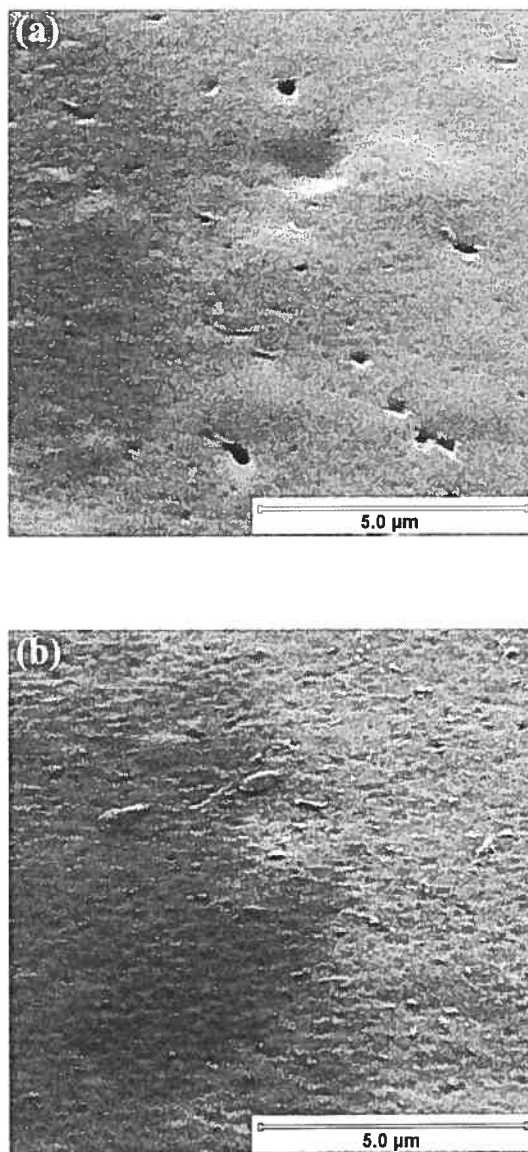


Figure 3.2. Scanning electron micrographs of the surface of the: (a) unmodified and (b) polyaniline modified CMX membranes.

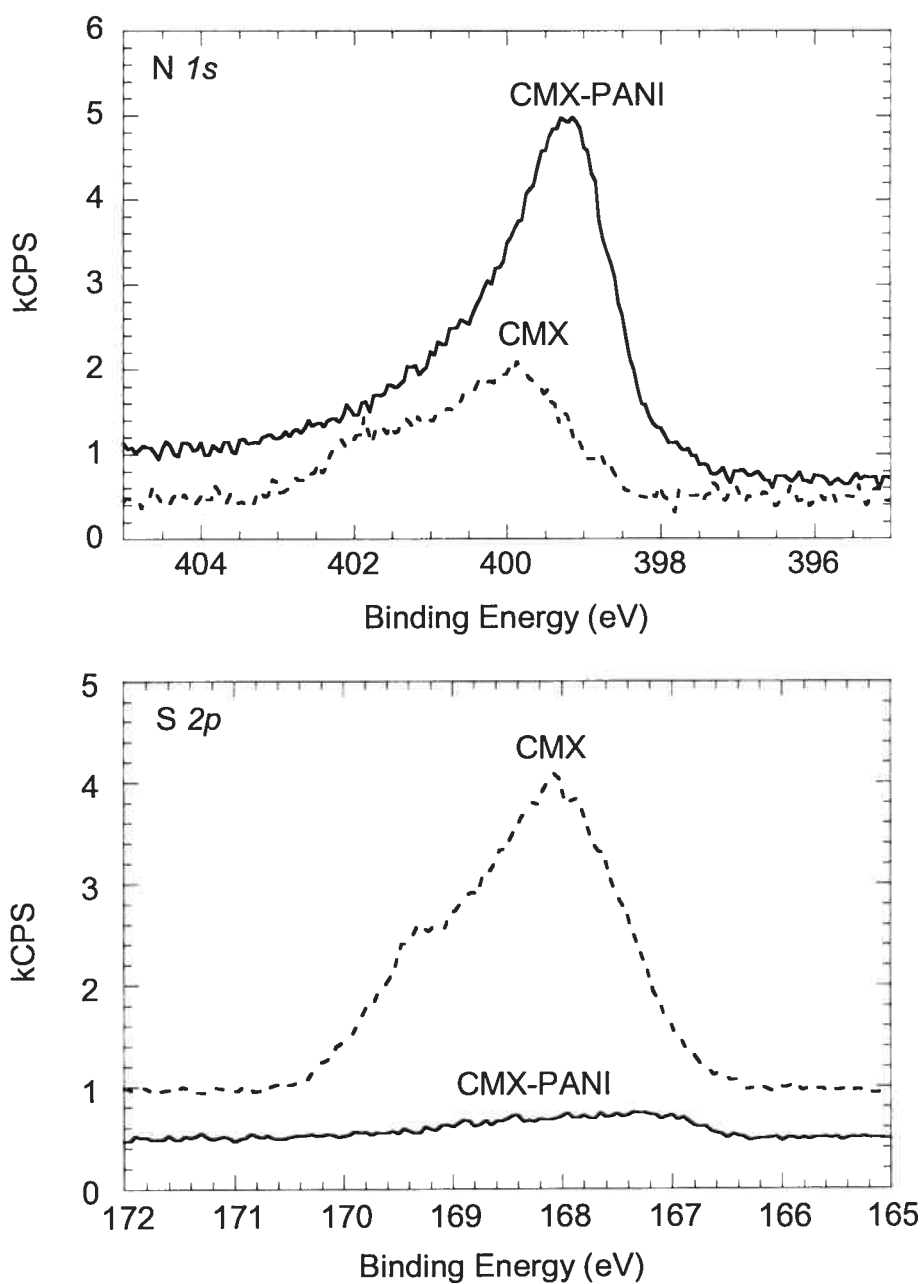


Figure 3.3. N 1s and S 2p core level spectra of unmodified and polyaniline modified CMX membranes.

3.4.2. Ion-Exchange Capacity (IEC)

The IEC values, defined as the number of millimoles of SO_3^- groups per gram of dry membrane, in its Na^+ form, can give an approximate amount of polycationic anilinium species exchanged with the Na^+ or H^+ ions in the membrane. Figure 3.4 shows a decrease in IEC from 1.48 meq/g to an average value of 1.41 meq/g for the CMX and CMX-PANI membranes respectively. The IEC for the unmodified CMX membrane is in close agreement with the values reported by the manufacturer ranging from 1.5 to 1.8 meq/g of dry membrane.¹⁷ The decrease in IEC can be related to the amount of the positively charged PANI replacing the counter-ions (Na^+ or H^+) of the sulfonate groups present in the modified membrane. The 5% decrease (or 0.07 meq/g) indicates the presence of a very little amount of PANI adsorbed on or within the membrane. In addition, Figure 3.4 shows that very little variation of IEC occurs for a time of immersion between 1 and 63 hours in the aniline solution. We can then assume that the maximum amount of anilinium species exchanged with the membrane's counter ions is reached very rapidly and this result can be correlated with the ones obtained by electrodialysis.

3.4.3. Electrodialysis (ED)

To evaluate the blocking effect of the positively charged PANI layer on the permeation of bivalent cations, the percentage metal leakage obtained after electrodialyses were compared for the CMX and CMX-PANI membranes. Figure 3.5 clearly demonstrates that the presence of a PANI layer reduces the Zn^{2+} leakage through the membrane from 10.1 to less than 1%. Similar results were obtained for the electrodialysis of solutions containing Cu^{2+} . Moreover, the immersion time in the aniline solution does not significantly affect the blocking efficiency of the membrane. This might suggest that the exchange between protons and anilinium ions is fairly complete after one hour (when using a 10% aniline in 1 M HCl solution).

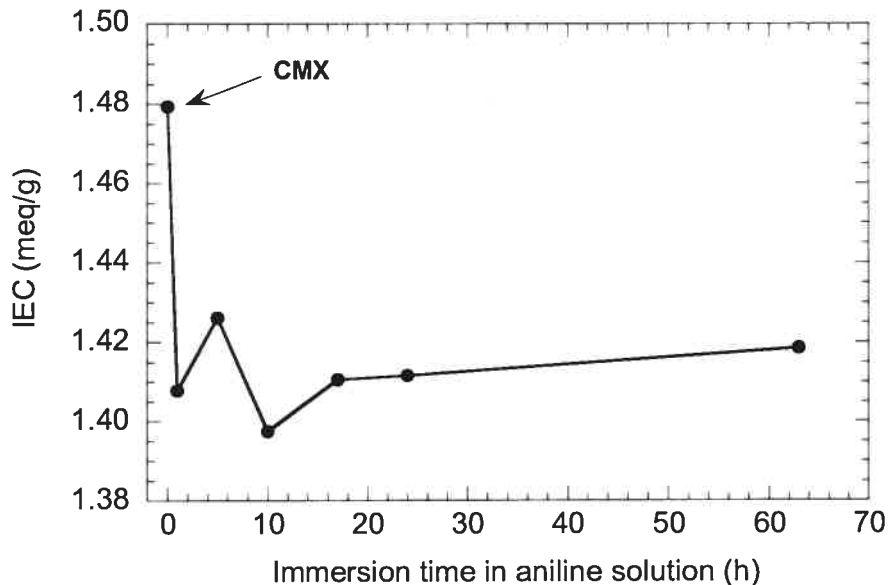


Figure 3.4. Ion-exchange capacity of unmodified and polyaniline modified CMX membranes as a function of the immersion time in a 10% aniline/1 M HCl solution. $t = 0$ corresponds to the unmodified membrane. The polymerization time is 1 hour.

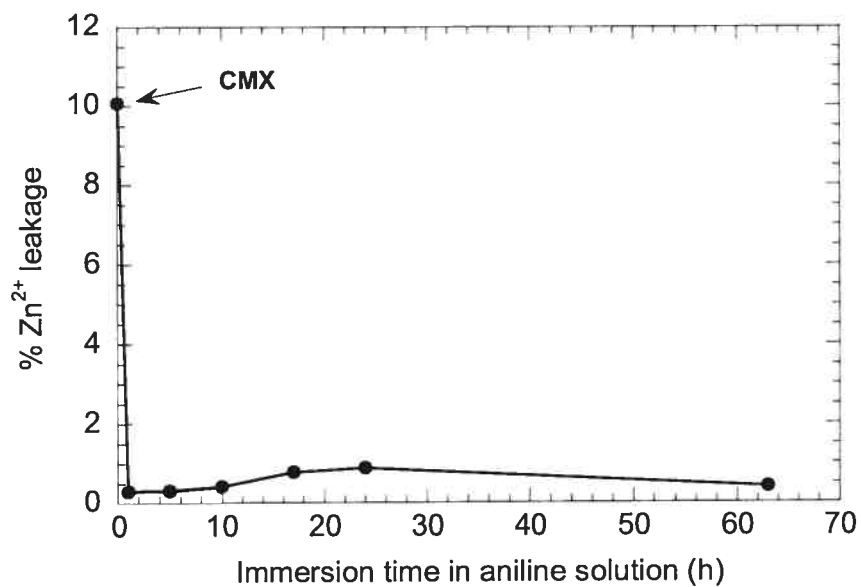
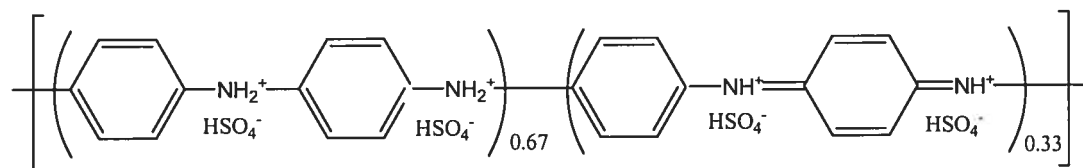


Figure 3.5. Percentage of Zn²⁺ leakage after electro dialysis of a 15 g/L Zn²⁺ in 0.5 M H₂SO₄ solution with the unmodified and polyaniline modified CMX membranes as a function of the immersion time in a 10% aniline/1 M HCl solution. $t = 0$ corresponds to the unmodified membrane. The polymerization time is 1 hour.

The low Zn^{2+} leakage through the PANI-modified CMX membranes is favorably comparable with those reported with a commercially available cation-exchange membrane (Neosepta CMS), designed specifically for high permselectivity to monovalent cations,⁹ and a polyethyleneimine (PEI) modified Nafion cation-exchange membrane⁸ for which the Zn^{2+} leakage was about 2-5 and below 1%, respectively. It should be noted that in these cases, other metallic cations (Mg^{2+} and Mn^{2+}) were present in the acidic solution and that their presence might influence the amount of leaking Zn^{2+} when compared to an acidic solution containing only Zn^{2+} . Finally, the Zn^{2+} leakage for a Nafion membrane (36%), which is reduced significantly with the PEI coating, is much higher than that of the unmodified CMX membrane that was used in the present investigation.

The procedure used for polyaniline formation is believed to yield the emeraldine base form.⁷ The emeraldine base is eventually doped by soaking in the protonic acid (H_2SO_4) which is used for the electro dialysis experiments. The pK_a values for the two acidic nitrogen atoms of PANI have been determined to be 2.5 ($-NH_2^+$) and 5.5 ($-NH^+=$).¹⁵ It should be noted that the imine groups act as a stronger base because steric hindrance of the adjacent phenyl ring disfavors the protonation of the amine groups.¹⁸ Thus, in the 0.5 M H_2SO_4 solution both groups should be protonated and a structure consistent with these values is given below:¹⁵



The presence of this cationic layer provides enhanced electrostatic repulsion for the divalent metallic cations and allows for the selective transport of protons.

In principle, the fully protonated PANI form that is obtained in highly acidic solution should contribute in a greater extent to this electrostatic repulsion than when PANI is used at neutral pH for which deprotonation is usually expected. Nonetheless, a good selectivity was reported for the separation of sodium and divalent calcium cations with a CMX-PANI membrane for electro dialysis in neutral solutions.⁷ According to Sata et al.⁷, this good permselectivity is attributed to the

fact that the PANI layer stays in its positively charged state, even during electro dialysis. Presumably, some trapped sulfonate groups of the CMX membrane can act as dopants and keep the protons within the PANI layer. This will maintain a fraction of positively charged polyaniline sites and could explain the good permselectivity of PANI in neutral solution. Interestingly, earlier studies have reported the use of trapped counter anions to extend the electroactivity of PANI to neutral and even basic solutions.¹⁹

3.5. CONCLUSION

The modification of a commercial cation-exchange membrane (CMX) with a thin protonated polyaniline layer led to a significant improvement for proton permselectivity in the presence of divalent zinc cations. These experiments were performed in a highly acidic solution that allowed the full protonation of the polyaniline layer. It would be interesting to investigate the contribution of the protonation to the barrier effect (for divalent cations) and consequently to discriminate between physical and electrostatic effects. Such experiments are currently underway in our laboratory.

3.6. ACKNOWLEDGEMENTS

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Chapitre 4

Characterization of a Cation-Exchange/Polyaniline Composite Membrane

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4.1. ABSTRACT

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 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. In order 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.

4.2. 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 sensors⁵ 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, 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 to permeate.

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 Ca²⁺ ions for electrodialysis in neutral solutions was reported by Sata *et al.*⁶ We have recently demonstrated that the Zn²⁺ and Cu²⁺ 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⁺ 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 ion 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 on 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.

4.3. EXPERIMENTAL SECTION

4.3.1. Chemicals

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (EM Science), HCl (EM Science), HNO_3 (EM Science), NaCl (BDH), H_2SO_4 (EM Science), $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ (Anachemia) and $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (Anachemia) were of A.C.S. reagent grade and used as received. Aniline (Aldrich) was distilled twice prior to use. Millipore water ($18 \text{ M}\Omega \cdot \text{cm}$) was used for the preparation of all solutions.

4.3.2. 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 of 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 (h) of immersion in the 10 % (v/v) aniline solution (1 h in

most cases), and Y for the time (h) 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.

4.3.3. *Electrodialysis (ED)*

Electrodialyses were performed in a two-compartment cell containing, in the anodic compartment, 150 mL of 15 000 ppm Zn(II) or Cu(II) in 0.5 M H₂SO₄ and in the cathodic compartment, 33 mL of 0.5 M H₂SO₄. The modified surface (surface: 5.1 cm²) was placed facing the anolyte. A current density of 100 mA/cm² was applied between two platinum plates during 3 h using a M273 Potentiostat/Galvanostat (EG & G Princeton Applied Research). The metal ion concentration in both compartments was determined by atomic absorption spectroscopy (Instrumentation Laboratory AA/AE Spectrophotometer model 257).

4.3.4. *Cyclic Voltammetry (CV)*

Prior to the preparation of electrodes, the CMX-PANI membranes were conditioned for at least one week in 0.5 M H₂SO₄. 16 mm² samples were then cut, slightly dried with a tissue and pressed into stainless steel grids (0.127 mm thickness) at 10 tons/cm² during 10 seconds. Both sides of the membrane were in contact with the grid. CV scans were carried out in a 0.5 M H₂SO₄ 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, a platinum grid. All potential values are reported versus Ag/AgCl.

4.3.5. *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 P₂O₅. XPS

analyses were performed using a VG Escalab 220i-XL system equipped with an 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^{-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 the 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 ± 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).

4.3.6. Scanning-Electron Microscopy (SEM)

Samples were dried under vacuum overnight at room temperature in the presence of P_2O_5 . Surface micrographs were taken using a Hitachi model S-2300 scanning electron microscope.

4.3.7. UV-Visible Spectroscopy

A 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 nm and 820 nm. Water was used as a blank. Samples were diluted 250 times in water.

4.3.8. 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 3 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 for 1 h at $65^\circ C$ 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).

4.4. RESULTS

4.4.1. Electrodialysis - Metal Leakage vs. Polymerization Time

Figure 4.1 illustrates how the percent metal leakage of Zn^{2+} and Cu^{2+} changes with polymerization time after electrodialysis. The metal ion 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^{2+} and 0.2 % for Cu^{2+}) after approximately 45-60 min of polymerization. Above 1 h of polymerization, the percent metal ion leakage increases up to values reaching 8 % for 10 h of polymerization.

4.4.2. Cyclic Voltammetry

Figure 4.2a 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 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 together and are more difficult to distinguish. Over one hour of polymerization, the signal of both redox couples nearly disappears. Figure 4.2b 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.

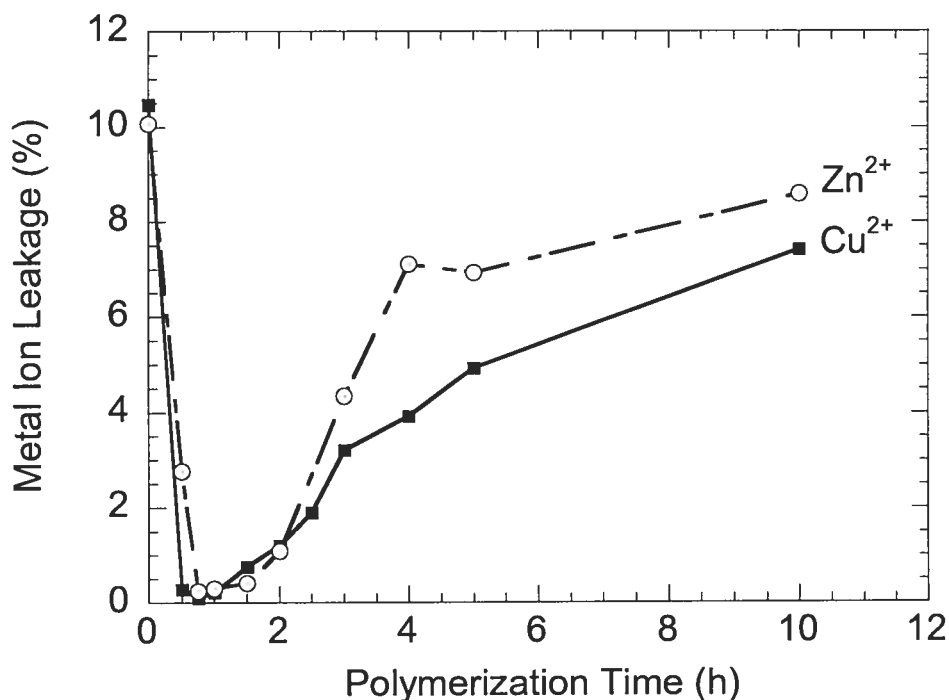


Figure 4.1. Percentage of zinc(II) and copper(II) ion leakage after electro dialysis of a 15 000 ppm Zn^{2+} or Cu^{2+} in 0.5 M H_2SO_4 solution with the unmodified and CMX-PANI composite membranes as a function of polymerization time. $t = 0$ corresponds to the unmodified membrane. It should be noted 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.

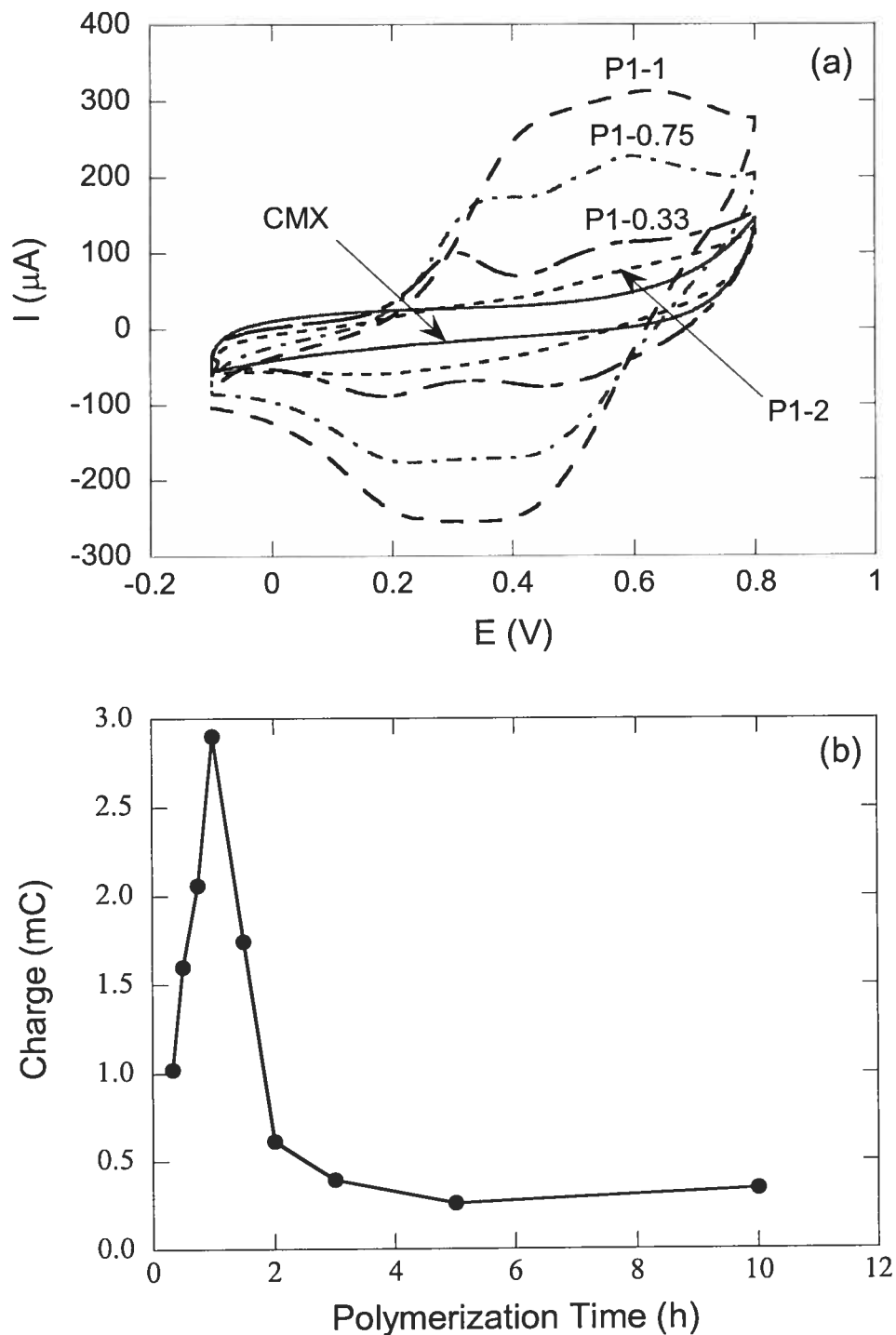


Figure 4.2. (a) Cyclic voltammograms in 0.5 M H_2SO_4 at 50 mV/s of the CMX and CMX-PANI membranes prepared with different polymerization time. Time of immersion in 10 % (v/v) aniline/1 M HCl solution was 1 h. (b) Corresponding charges integrated from the oxidation peaks as a function of polymerization time.

4.4.3. X-ray Photoelectron Spectroscopy

4.4.3.1. Survey Spectra

XPS has been extensively used to study the different oxidation states of PANI.¹³⁻¹⁵ Figure 4.3 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 (SO₃⁻) groups; 284.6 eV (C 1s) from the main polymer chains; 271 eV (Cl 2s) and 200 eV (Cl 2p) attributed to the poly(vinyl chloride) support. A small N 1s peak is also detected at 400 eV on the unmodified CMX membrane which is 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.

4.4.3.2. Core Level Spectra

The Cl 2p, S 2p and N 1s core level spectra are described below. Table 4.1 gives the elemental composition and the relevant ratio values determined from the core level spectra. The evolution of these atomic concentrations is discussed below.

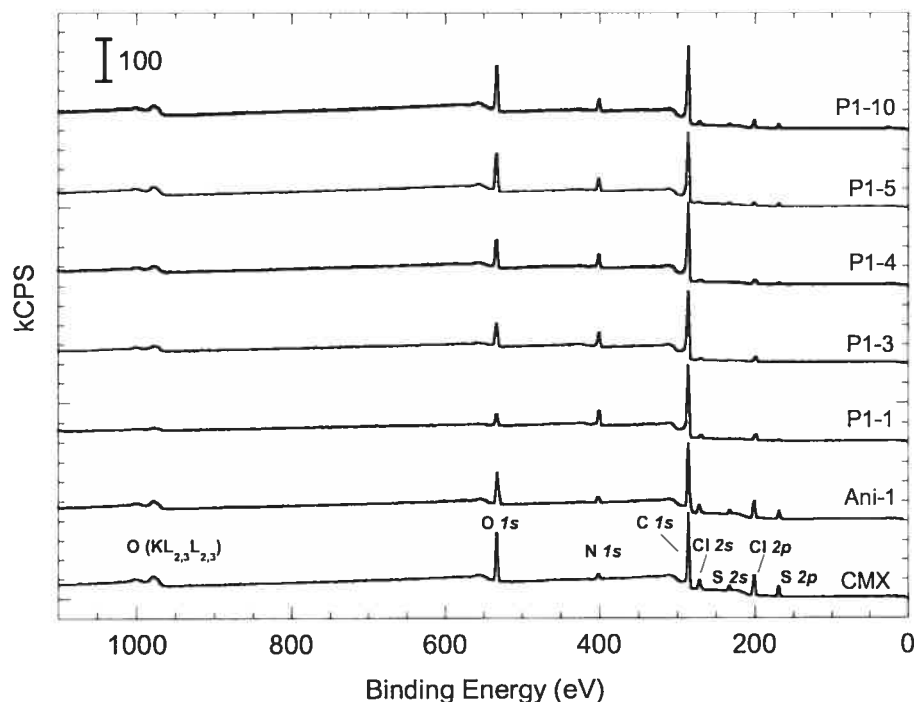


Figure 4.3. XPS survey spectra of the unmodified CMX, Ani-1 (membrane ion-exchanged with anilinium ions for 1 h using a 10 % (v/v) aniline in 1 M HCl solution) and CMX-PANI membranes prepared with different polymerization times.

Table 4.1. Elemental composition of the unmodified CMX, CMX ion-exchanged with anilinium species, and CMX-PANI composite membranes determined by XPS.

| Element (%) | CMX | ANI-1 | P1-0.5 | P1-0.75 | P1-1 | P1-3 | P1-4 | P1-5 | P1-10 |
|--------------------------|------|-------|--------|---------|-------|-------|------|------|-------|
| Cl (PVC) | 8.8 | 6.6 | 1.8 | 0.92 | 0.47 | 0.59 | 0.87 | 1.4 | 2.6 |
| Cl (ionic) [†] | 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) [‡] | 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* | | 0 | 0.27 | 0.29 | 0.40 | 0.28 | 0.22 | 0.07 | 0.09 |
| N/S* | 0 | 0.29 | 2.81 | 5.02 | 13.30 | 11.36 | 8.02 | 3.64 | 2.57 |

[†] PVC contribution removed and both ionic doublet included (Cl $2p_{3/2}$ centered at 197.8 and 199.4 eV). [‡] 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:

$$\%N(\text{CMX})_{\text{sample}} = (\%S_{\text{sample}} / \%S_{\text{CMX}}) \times \%N(\text{total})_{\text{sample}}^{**}$$

*Nitrogen from PANI only. **Note: It is demonstrated in section 5.4.2 that the %N (PANI) is underestimated when using this calculation method but this does not affect the interpretation of the data given in this chapter.

Cl 2p. The Cl $2p$ spectra for the CMX and CMX-PANI membranes are depicted in Figure 4.4. 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 envelop 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 re-appear. The covalent and ionic chlorine content are presented in Table 4.1. 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) (Annexe I, Figure I-1).

S 2p. The large peak observed at 169 eV (Figure 4.5) for 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 centres are found at 168.9 and 170.1 eV corresponding to the $2p_{3/2}$ and $2p_{1/2}$ contributions (Annexe I, Figure I-2). Figure 4.5 and Table 4.1 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 re-appearance of this latter group.

N 1s. The N $1s$ spectra for the different membranes are represented in Figure 4.6. As specified above, the 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 towards higher binding energy. For the membranes prepared at longer polymerization times, the spectra resemble that of the bare CMX membrane.

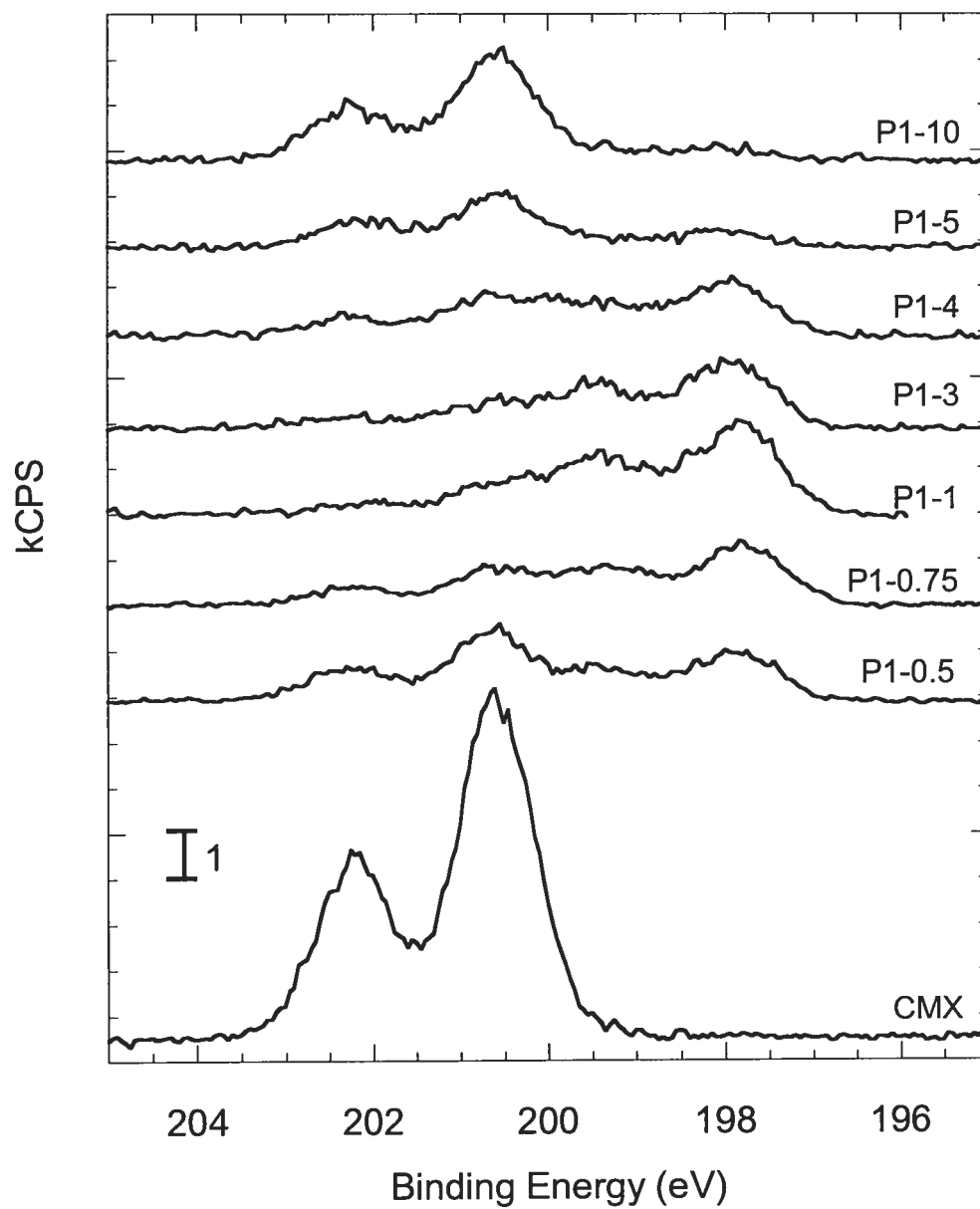


Figure 4.4. Cl $2p$ core level spectra of the unmodified CMX and CMX-PANI membranes prepared with different polymerization times.

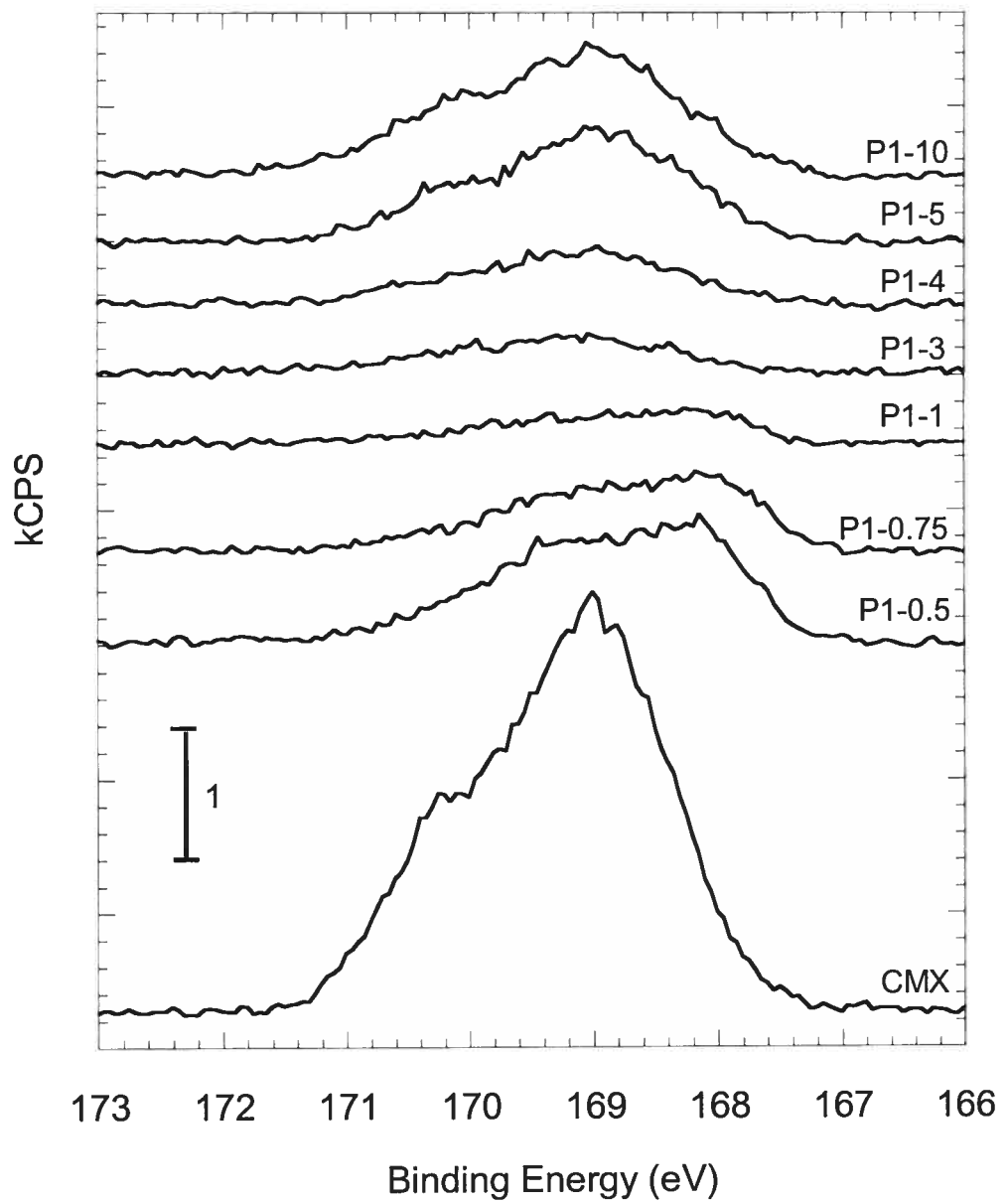


Figure 4.5. S 2*p* core level spectra of the unmodified CMX and CMX-PANI membranes prepared with different polymerization times.

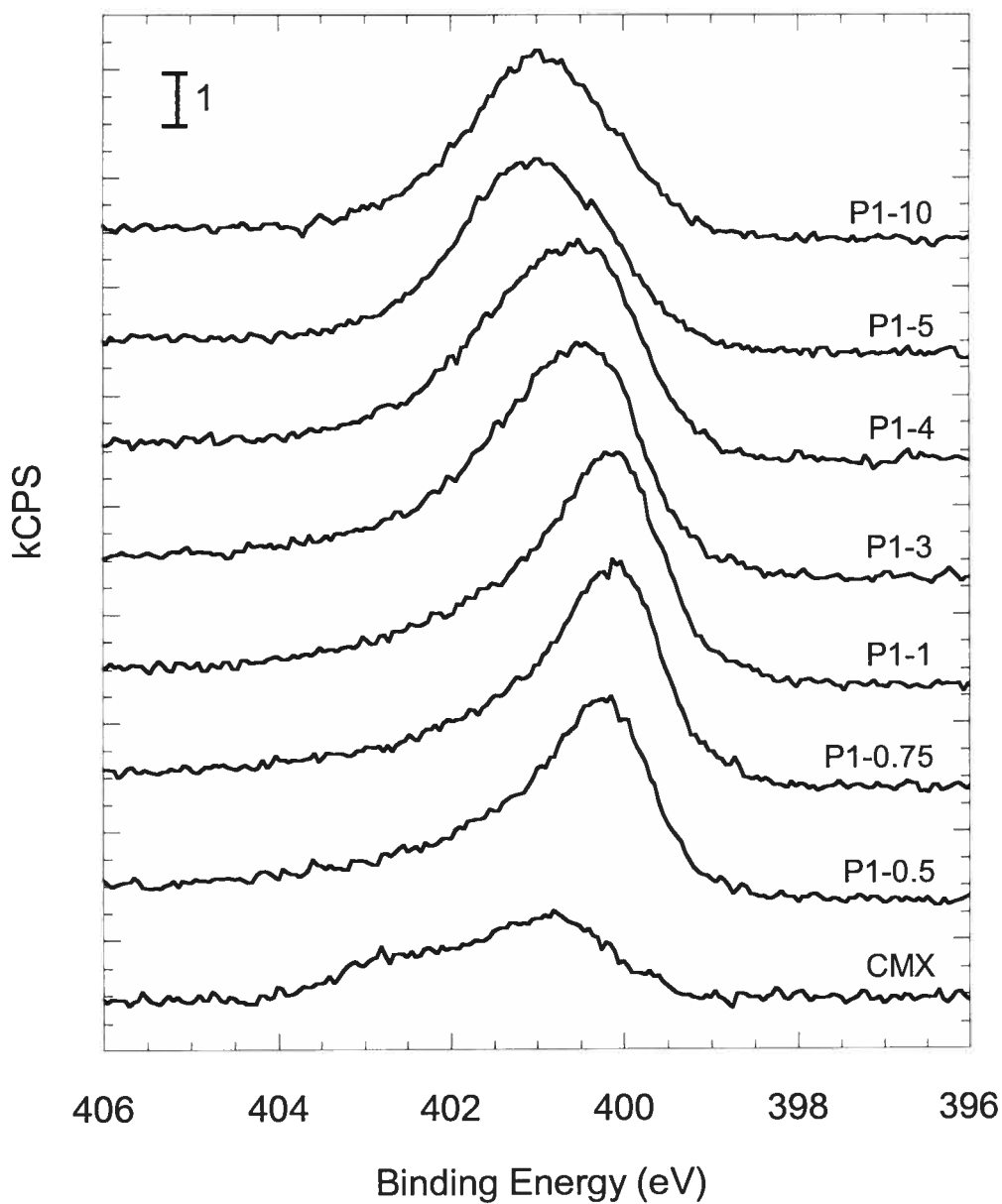


Figure 4.6. N 1s core level spectra of the unmodified CMX and CMX-PANI membranes prepared with different polymerization times.

4.4.4. Ion-Exchange Capacity

In order 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 membranes prepared at various polymerization times (Figure 4.7). 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 4.1). 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 ion leakage which shows a minimum at a polymerization time of about 1 h.

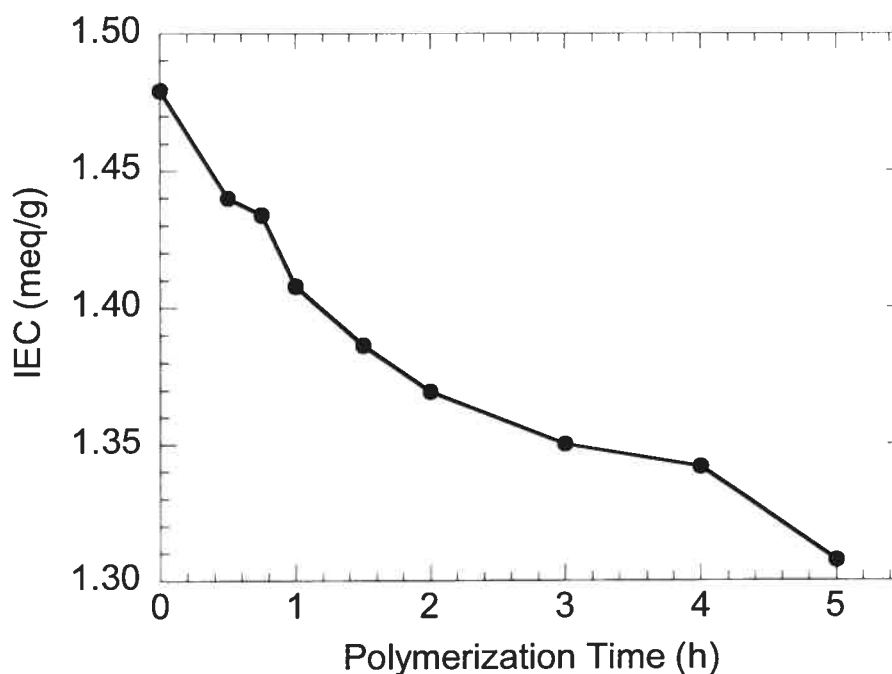
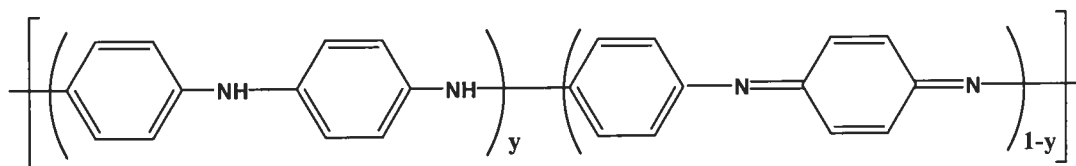


Figure 4.7. Ion-exchange capacity of unmodified (at $t=0$) and CMX-PANI composite membranes as a function of the polymerization time. Time of immersion in 10 % (v/v) aniline/1 M HCl solution was 1 h.

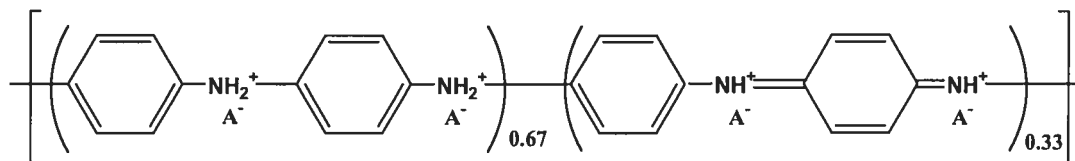
4.5. DISCUSSION

The chemical composition of the surface of the membrane clearly changes as the polymerization time increases. One consequence of the change is that a minimum metal ion leakage is obtained after 45-60 min of polymerization. With a polymerization time shorter than 1 h, the decrease in metal ion 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 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. Sata *et al.*⁶ 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, in our experimental conditions, either Cl^- , HSO_4^- 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.*⁶ have evaluated the electronic conductivity and the doping level of PANI as a function of polymerization time. They have demonstrated an optimal conductivity at 1 h and that over 10 h, PANI can no longer be doped with bromide indicating that an 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 derived from the XPS spectra. First, when comparing the Ani-1 and P1-1 survey spectra (Figure 4.3), significant differences in peak intensity for N $1s$ are noticeable, even though the immersion time in the aniline solution was 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 signal for P1-1 suggests that upon polymerization on the membrane, anilinium ions diffuse towards 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, $S_2O_8^{2-}$, towards the bulk of the membrane. These phenomena favour polymerization at the surface of the membrane.

Secondly, the Cl $2p$ (Figure 4.4), S $2p$ (Figure 4.5) and N $1s$ (Figure 4.6) core level spectra demonstrate that upon polymerization, the peaks associated to 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 4.1 shows that the maximum nitrogen concentration and the lowest chlorine (from PVC) and sulfur (sulfonate) concentration are reached after 1 h of polymerization. The presence of PANI yielding 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 (Figures 4.2a and 4.2b). 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 electro dialysis.

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 4.8, 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 since XPS and SEM data showed that no polyaniline is found on the reverse side of the 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 4.5 shows that the S $2p$ peak is displaced toward lower binding energy after one hour of polymerization (168.3 eV and 169.6 eV for S $2p_{3/2}$ and S $2p_{1/2}$, respectively) in comparison to the bare CMX (168.9 eV and 170.1 eV for S $2p_{3/2}$ and S $2p_{1/2}$, respectively) (Annexe I, Figure I-2 and Table I-2). Interactions between the positively charged imine/amine groups from PANI and the sulfonate groups could explain this displacement. In fact, neutral sulfonate groups

(SO₃H) have a lower electron density, and consequently a higher binding energy, than the SO₃⁻ interacting with =NH⁺- and/or -NH₂⁺- groups.^{19,20}

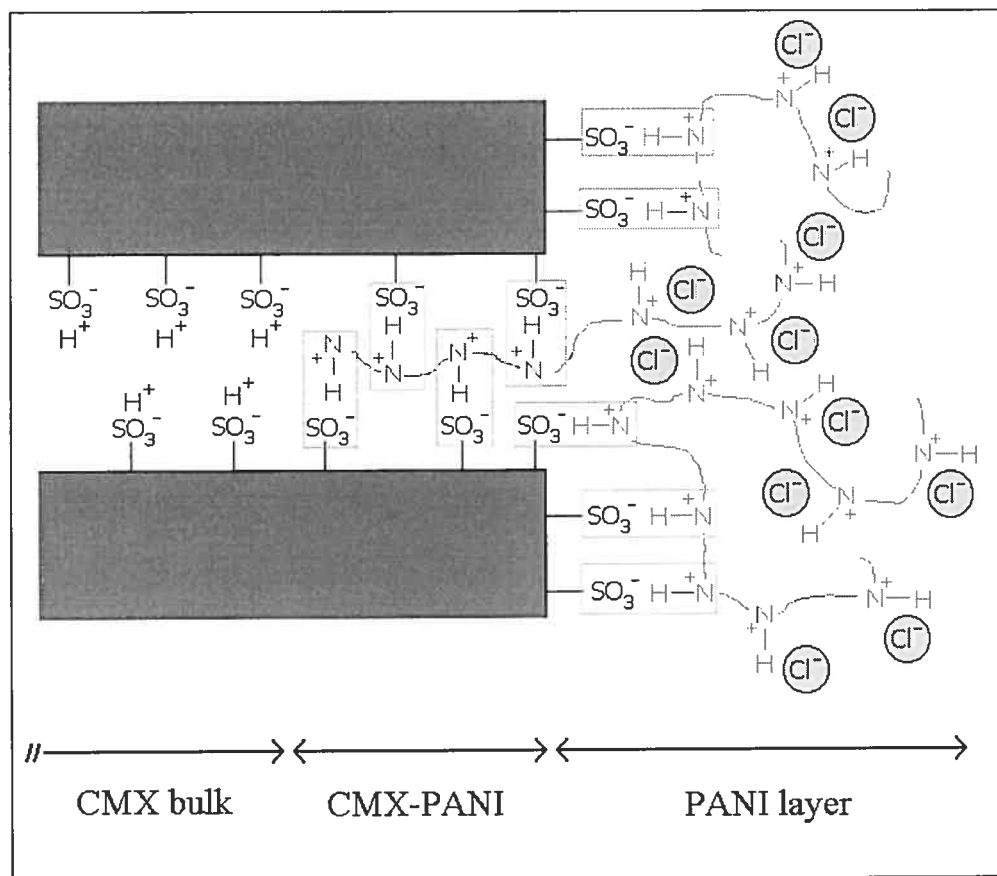
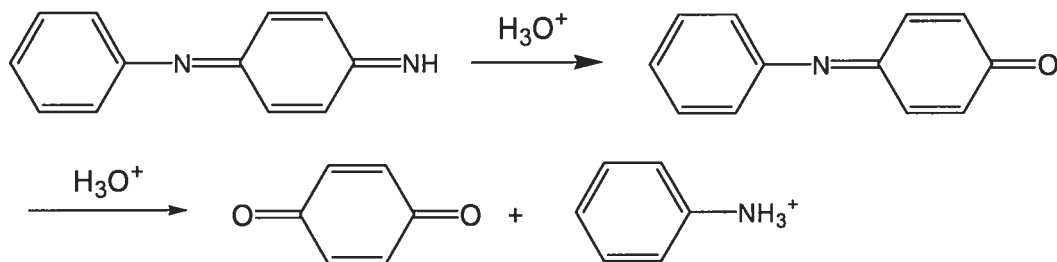


Figure 4.8. Idealized schematic representing the three different layers found on a CMX-PANI composite membrane. This is a representation for the membrane showing the best permselectivity for our experimental conditions.

When the polymerization time is extended over 1 h, a drop in CMX-PANI permselectivity (Figure 4.1) and electroactivity (Figure 4.2) occurs. Possible explanations for these data could be either the overoxidation of PANI into its non-conductive 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 and CV. Thus, the same techniques were used in this study to detect BQ. The cyclic voltammograms represented in Figure 4.2a 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 4.9a 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 4.9b). Afterwards, 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 4.1) since the PANI layer still possesses a blocking behaviour towards bivalent cations at polymerization times over 1 h while no more electrochemical activity is found by CV. This could be explained by the fact that the CV experiments only allows the detection of the fraction of conducting PANI in direct and close contact with the stainless steel grid. The thickness of the CMX-PANI membrane being probed, under our experimental conditions, corresponds to the diffusion layer

which can be estimated to be 50 μm when using a diffusion coefficient of $1 \times 10^{-10} \text{ m}^2/\text{s}$. However, it is believed that at long polymerization times, the PANI chains no longer form a continuous network at the surface of the membrane and are most likely found in a higher oxidation state, which is less conducting.

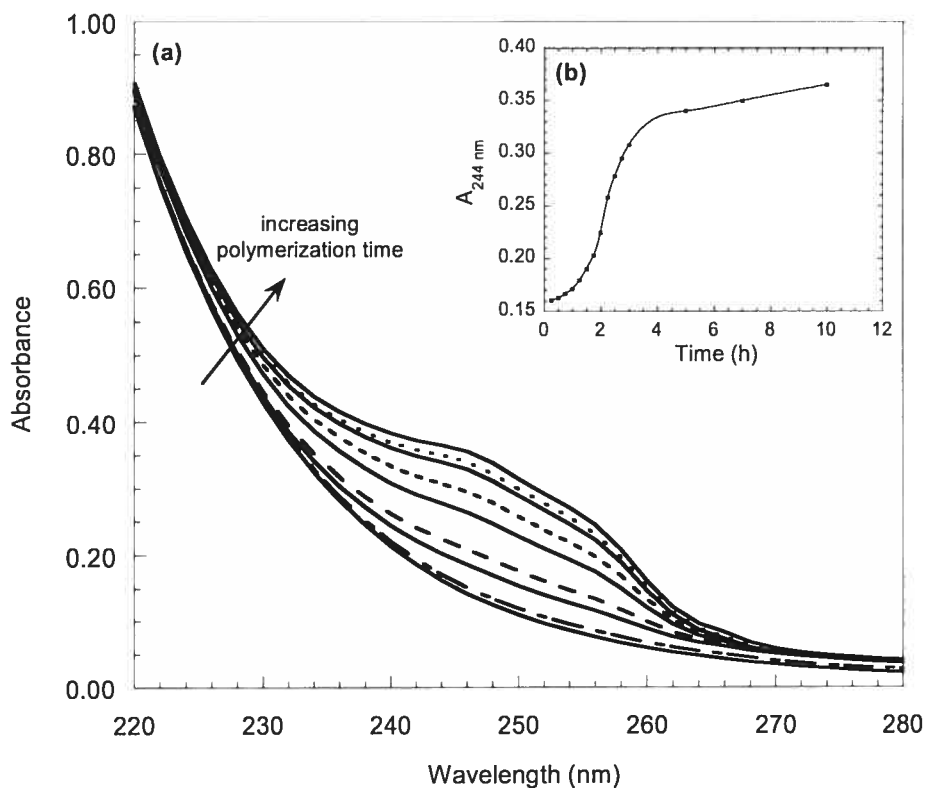


Figure 4.9. (a) UV-visible spectra of the 1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution taken in the reagent compartment after various polymerization time. Time of immersion in 10 % (v/v) aniline/1 M HCl solution was 1 h. (b) Corresponding absorbance recorded at 244 nm as a function of polymerization time.

The XPS study allows a better understanding of the phenomenon occurring above 1 h of polymerization. Beyond this oxidation time, the Cl $2p$ (Figure 4.4), S $2p$ (Figure 4.5) and N $1s$ (Figure 4.6) spectra exhibit a gradual return to the spectra corresponding to the unmodified membrane (see also Table 4.1). Subsequently, the decrease in electrochemical activity as well as the permselectivity properties seems

to be explained by the progressive loss of the PANI layer due to its degradation into BQ. These data are confirmed by SEM (Annexe I, Figure I-3). The photomicrographs 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 4.8 would be almost completely degraded. The fact that some nitrogen is still detected (Table 4.1) and that the Cl $2p$ (Figure 4.4), S $2p$ (Figure 4.5) and N $1s$ (Figure 4.6) spectra of the CMX membrane are not totally recovered after 10 h of polymerization indicates that a very thin or non-uniform PANI layer remains present. The PANI left on or within the membrane might contribute to partially block the bivalent cations transport since the metal ion leakage for P1-10 is not as high as for the bare CMX. Also, the removal of most of the first PANI layer (Figure 4.8) might also justify the lowering of the Cl/N ratio observed in Table 4.1. 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 towards higher binding energies (Figure 4.5) 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 Sata⁶ would also be explained by this gradual degradation of PANI. 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 in 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 towards higher binding energy (Figure 4.6) 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 ion leakage observed in Figure 4.1. However, Figure 4.7, 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 fibres 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 4.8), the thin surface

layer is degraded into BQ as the oxidation time is increased. In the meantime, longer fibres are formed inside the CMX which would result in decreasing the IEC values. The formation of oligomers and/or PANI fibres towards the bulk of the membrane cannot be detected by CV nor XPS since they are located too far from the surface. Only the ends of the chains of these oligomers and/or fibres located near the surface would be detected. Moreover, these oligomers and/or fibres do not provide an efficient blocking barrier for bivalent cations, as demonstrated by the ED results (Figure 4.1), 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.

4.6. 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 membranes 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

4.7. ACKNOWLEDGMENTS

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4.8. INFORMATION AVAILABLE IN ANNEXE I

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 are available in Annexe I.

4.9. REFERENCES

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Chapitre 5

Chemical Polymerization of Aniline on a Poly(Styrene Sulfonic Acid) Membrane: Controlling the Polymerization Site Using Different Oxidants

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5.1. ABSTRACT

Poly(styrene sulfonic acid) membranes (Neosepta CMX, Tokuyama Corp.) have been modified by *in situ* polymerization of aniline. $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 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, electro dialysis, 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+} .

5.2. 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, metals, silicon, and nanoparticles. Also, both polyaniline and polypyrrole have been used to prepare membrane composites used in different applications¹ including gas permeation,^{2, 3} pervaporation,⁴ fuel cells,⁵⁻⁷ and selective ion transport.⁸⁻¹³

Cation exchange membranes are used in several electrochemical techniques such as fuel cells, electrolyses, and electro dialysis. 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 electro dialysis 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 as a function of the PANI layer location but could also be useful for applications, such as in fuel cells, which require a conducting polymer layer only in the middle of the membrane or on one surface of the membrane. Indeed, the presence of a conducting polymer, crossing over the whole membrane in a fuel cell, can short-circuit the cell.

In this paper, we 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.

5.3. EXPERIMENTAL SECTION

5.3.1. Materials

$\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ (Aldrich), KIO_3 (EMD), HCl (EMD), H_2O_2 (EMD), H_2SO_4 (EMD), NaCl (BDH), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (BDH), and $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ (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 Ω 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 5.1.¹⁴ The membrane was stored in 0.5 M NaCl prior to its use.

Table 5.1. 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 μm |
| Exchange Capacity | 1.5-1.8 meq/g Na-form dry membrane |
| Water Content | 0.25-0.30 g H ₂ O/g Na-form dry membrane (equilibrated in 0.5 M NaCl) |
| Electric Resistance | 2.5-3.5 Ωcm^2 (equilibrated in 0.5 M NaCl, at 25°C) |

5.3.2. 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 cm²). 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 were 1 M aniline diluted in 1 M HCl solution and 0.3 M oxidant diluted in water or in 0.01 M HCl for FeCl₃ solutions. The modified membranes were stored either in 1 M HCl or in 1 M H₂SO₄ solutions. The membrane identification is as follows: PXS-Y where P stands for polyaniline, X, the number of steps (S), and Y, the oxidant.

5.3.3. Scanning Electron Microscopy (SEM)

Membranes were conditioned in 1 M HCl and were dried under vacuum overnight at room temperature in the presence of P₂O₅. 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.

5.3.4. 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 P₂O₅. XPS analyses were performed using a VG Escalab 220i-XL system equipped with a hemispherical analyzer and an Al anode (K α 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 C 1s at 284.6 eV after deconvolution. Curve fitting and peak integration were carried out using the CasaXPS (version 2.1.25) software. After a Shirley background correction, all peaks were deconvoluted by assuming a Gaussian-Lorentzian line shape. For the deconvolution of the Cl 2p and S 2p 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 Cl 2p_{1/2}-Cl 2p_{3/2} and S 2p_{1/2}-S 2p_{3/2} peaks. The surface atomic composition was calculated using the high-resolution spectra and the appropriate relative 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).

5.3.5. 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 P₂O₅. Sample analysis was performed on a Fisons Instruments SPA, model EA1108.

5.3.6. Ion-Exchange Capacity (IEC)

All membranes were washed and stabilized in 1 M HCl, H₂O 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 P₂O₅ 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).

5.3.7. 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 % H₂O and λ , the number of moles of H₂O per moles of sulfonic acid groups (SO₃⁻), were determined according to the following equations:

$$\%H_2O = \frac{m_{\text{wet membrane}} - m_{\text{dry membrane}}}{m_{\text{wet membrane}}} \times 100 \quad (5.1)$$

$$\lambda = \frac{\frac{m_{\text{wet membrane}} - m_{\text{dry membrane}}}{m_{\text{dry membrane}}} / 18gH_2O / mol}{IEC} \quad (5.2)$$

where m is the mass (g) and IEC is the ion-exchange capacity (moles SO₃⁻ per g of dry membrane).

5.3.8. Electrodialysis

Electrodialyses were performed in a two-compartment cell containing, in the anodic compartment, 150 mL of 1.5 g/L Zn^{2+} 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 out under a nitrogen flow. The metal concentration in both compartments was determined by atomic absorption spectroscopy (Varian SpectraAA 220FS). From these concentrations, the % Zn^{2+} leakage is calculated according to the following equation, where m is the mass (g):

$$\%Zn^{2+} \text{ leakage} = \frac{m_{Zn^{2+}}(\text{catholyte})}{m_{Zn^{2+}}(\text{catholyte}) + m_{Zn^{2+}}(\text{anolyte})} \times 100 \quad (5.3)$$

5.3.9. Conductivity Measurements

Measurements were carried out at room temperature (23 ± 1) $^{\circ}C$ 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 μm . The solution ionic resistance was

measured using the same setup, and its value was subtracted from the resistance values measured to calculate the membrane resistance and conductivity values.

5.4. RESULTS

5.4.1. Chemical Polymerization of Aniline

The chemical polymerization of aniline was 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 5.1. In the one-step method, the anilinium (or positively charged aniline) solution was 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 was first added in one compartment and water in the second compartment. Then, the aniline solution was replaced by the oxidant solution after rinsing the compartment with water. This two-step modification was intended to favor the modification on only one side of the membrane.

After modification, the membrane turns green-blue which indicates the presence of polyaniline. After dipping the membrane into an acidic solution (HCl or H₂SO₄) for several hours, the PANI layer is in its emeraldine salt form, the doped and conductive form of polyaniline.¹⁵ The appearance of the green-blue layer was observed for all the membranes prepared using (NH₄)₂S₂O₈ and FeCl₃ as oxidants. When using H₂O₂, 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}

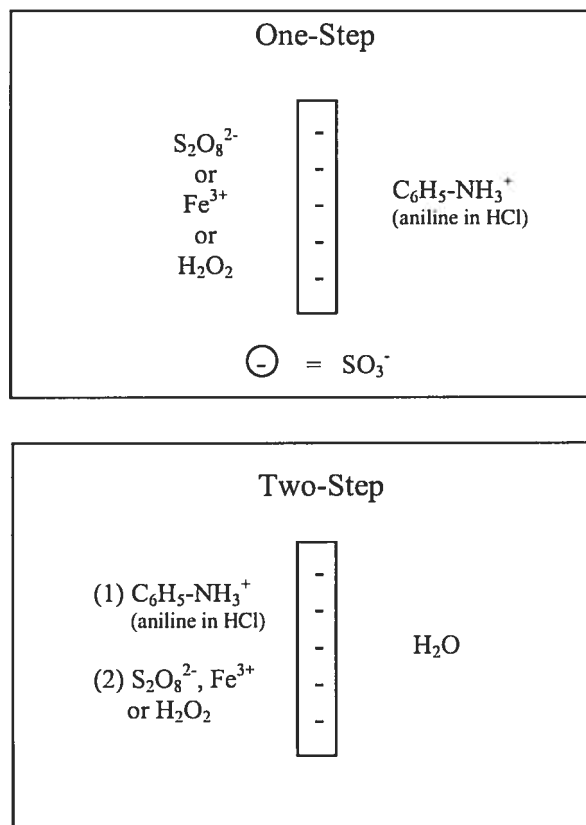


Figure 5.1. Membrane modification methods using a two-compartment Teflon[®] cell: one-step versus two-step procedures.

5.4.2. 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 5.2 illustrates the SEM images of the bare and modified membranes using both the one-step and two-step methods. The bare membrane (Figure 5.2a) shows a rather smooth surface when compared to the membrane modified using $(NH_4)_2S_2O_8$ in one

step (Figure 5.2b). 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 5.2c) and H_2O_2 (Figure 5.2d) in one step, 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Figure 5.2e) and FeCl_3 (Figure 5.2f) both result in a PANI coating and no change in morphology was observed with H_2O_2 treatment (Figure 5.2g).

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 N *1s* core level spectra of polyaniline can be defined by at least three peaks centered at 398.2, 399.4, and > 400 eV attributed to quinoid imine ($-\text{N}=\text{}$), benzenoid amine ($-\text{N}-$), and positively charged nitrogen (N^+), respectively. For the CMX membrane, Figure 5.3a 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 (Figure 5.3b). 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 N *1s* spectra of the unmodified CMX and the $\text{P1S-S}_2\text{O}_8^{2-}$ 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 N *1s* 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.

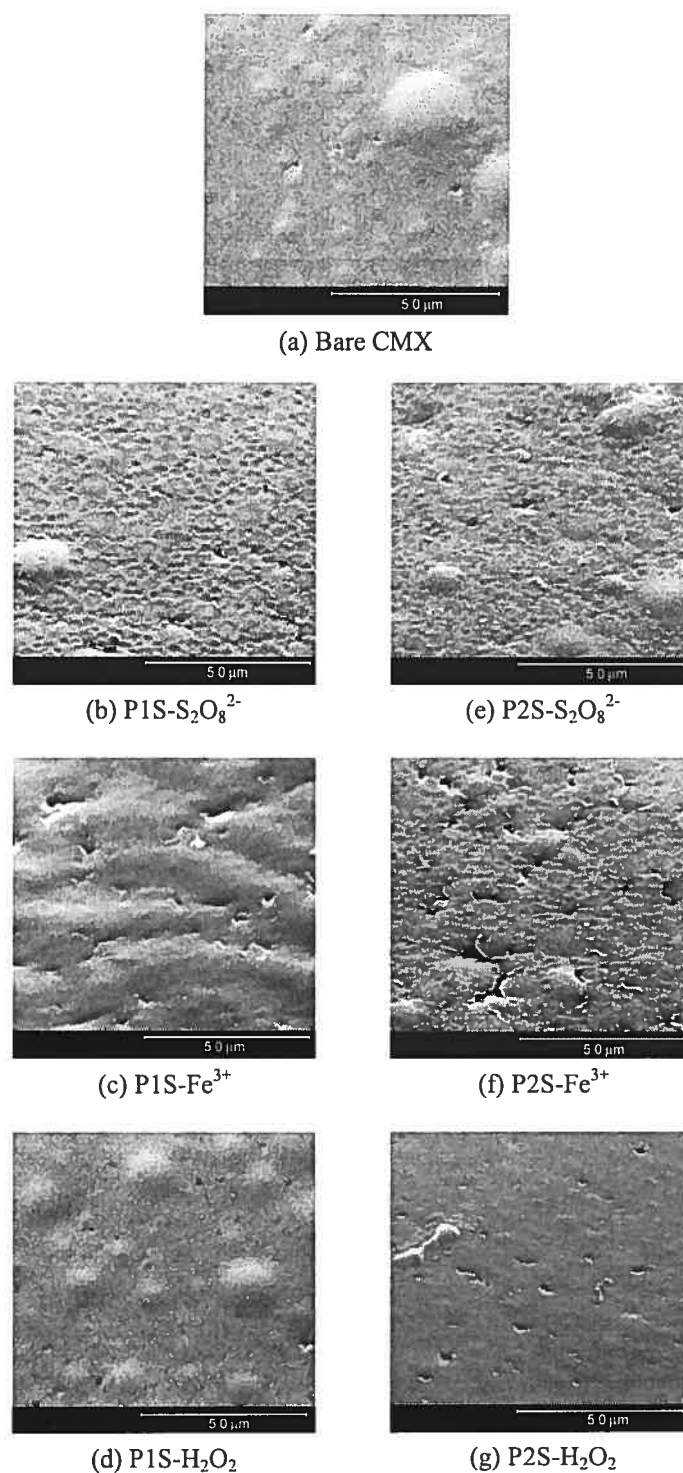


Figure 5.2. Scanning electron microscopy (SEM) micrographs of the bare and modified CMX membranes. The surface shown is the side that was exposed to the oxidant during the modification procedures. The bar scale represents 5 μm.

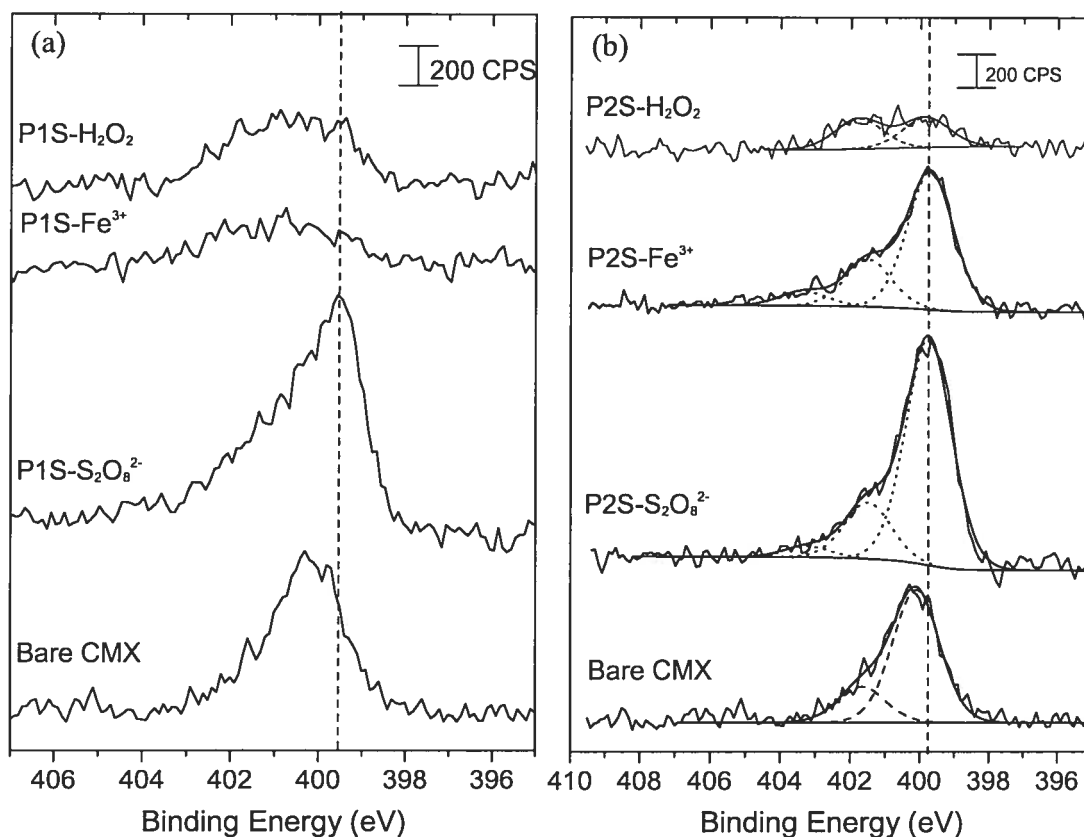


Figure 5.3. N $1s$ core level spectra of the bare and modified CMX membranes using the one-step method (a) and two-step method (b). The surface shown is the side that was exposed to the oxidant during the modification procedures. The curve fitting of P2S- $S_2O_8^{2-}$ and P2S- Fe^{3+} do not include the CMX nitrogen contribution (refer to text for details).

Nonetheless, the P1S- $S_2O_8^{2-}$ N $1s$ 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. 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 ($-NH^+=$, $pK_a = 5.5$) are more easily protonated than the amine groups ($-NH_2^+$, $pK_a = 2.5$) and the membranes were conditioned in 1 M HCl.^{20, 22} Consequently, it is plausible to assume that all membranes with a N $1s$ spectra which can be deconvoluted into three

components at 399.7, 401.4 and above 403 eV have a PANI layer at their surface. Hence, in addition to P1S-S₂O₈²⁻, PANI characteristic peaks were also found on P2S-S₂O₈²⁻ and P2S-Fe³⁺ (Figure 5.3b), which is consistent with the results obtained by SEM. The P1S-H₂O₂ N 1s spectrum (Figure 5.3a) was similar to the P1S-Fe³⁺ (Figure 5.3a) and the P2S-H₂O₂ spectra (Figure 5.3b) 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-Fe³⁺ and P1S-H₂O₂ N 1s spectra. The degradation in nitrogen was also observed by XPS with membranes solely treated with the oxidants (Table 5.2).

Table 5.2. XPS and elemental analysis results of membranes treated solely with the oxidant using the one-step method (1 hour reaction).

| | XPS | | Elemental Analysis | |
|---|---------|---------|--------------------|-----------|
| | at. % N | at. % S | wt. % N | wt. % S |
| Bare CMX | 3.4 | 5.0 | 0.61 ± 0.07 | 5.1 ± 0.6 |
| CMX S ₂ O ₈ ²⁻ | 2.0 | 5.0 | 0.60 | 4.9 |
| CMX Fe ³⁺ | 2.4 | 5.4 | 0.57 | 5.0 |
| CMX H ₂ O ₂ | 2.0 | 4.8 | 0.54 | 5.3 |

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 5.3, the % N increases in the following order: P1S-S₂O₈²⁻ ≤ P2S-Fe³⁺ < P2S-S₂O₈²⁻. Even if the % N are only estimated values, they are sufficiently reliable for the purpose of our study.

Table 5.3. XPS analysis of the surface of the unmodified and modified CMX membranes.

| | % N | % 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 | | | |

*The CMX nitrogen contribution was not subtracted to the nitrogen values used in the data reported in this table.

The deconvoluted S $2p$ core level spectra for the membranes studied are presented in Figure 5.4a. The unmodified CMX membrane shows the presence of a doublet at 168.2 eV (S $2p_{3/2}$) and at 169.4 eV (S $2p_{1/2}$) 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 N $1s$ (CMX), the S $2p$ 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 at lower binding energies, that is, at 167.4 and 168.7 eV for the S $2p_{3/2}$ and S $2p_{1/2}$ 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-S₂O₈²⁻ and P2S-Fe³⁺ (Figure 5.4b) S $2p$ spectra also show the presence of the two S $2p$ doublets as for the P1S-S₂O₈²⁻ (Figure 5.4a). On the other hand, the P2S-H₂O₂ (Figure 5.4b) spectra is similar to the P1S-H₂O₂ and P1S-Fe³⁺ spectra (Figure 5.4a), that is, displaying a single doublet indicating the absence of PANI. The data obtained with the S $2p$ spectra are consistent with the N $1s$ spectra and the SEM images.

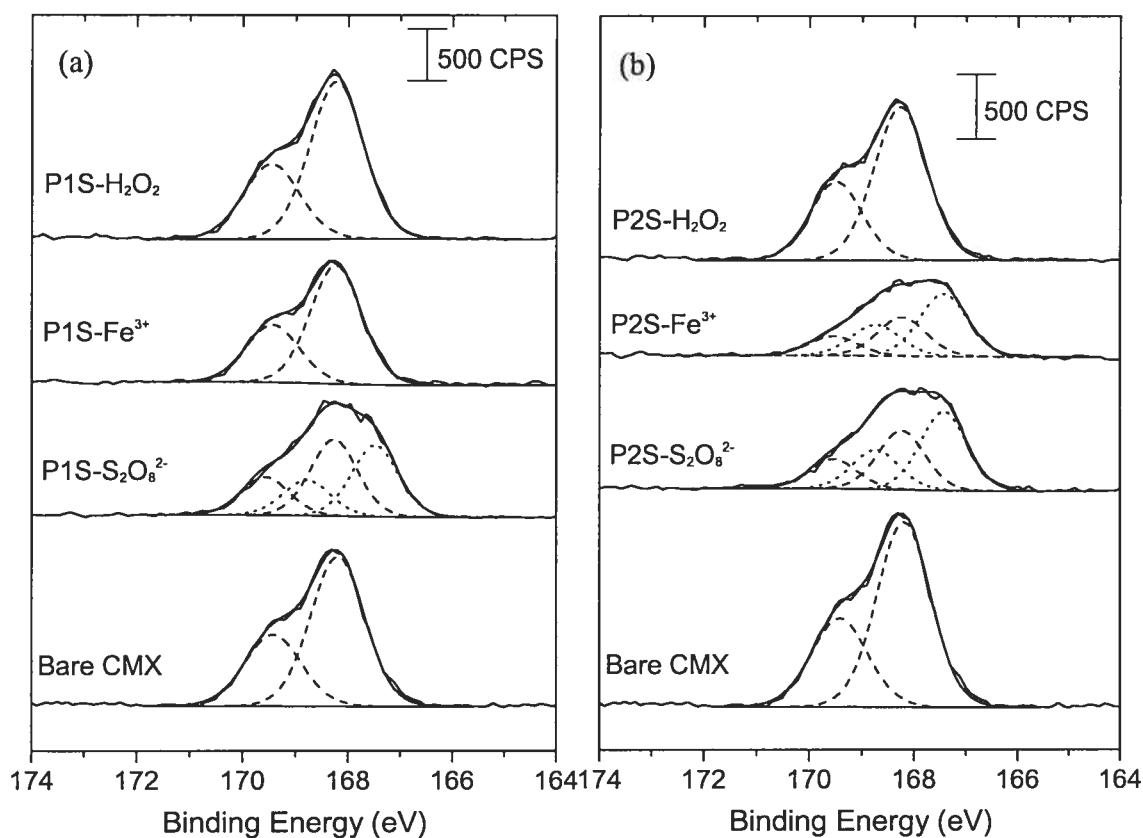


Figure 5.4. Curve fitted S $2p$ core level spectra of the bare and modified CMX membranes using the one-step (a) and two-step (b) methods where (...) represents the SO_3^- groups interacting with PANI^+ and (---), the SO_3^- with an H^+ counterion. The surface shown is the side that was exposed to the oxidant during the modification procedures.

From the S $2p$ 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, $S_{\text{PANI}^+}/S_{\text{total}}$. For the membranes covered with a PANI layer, these ratios were found to be 0.49, 0.57, and 0.62 for the P1S- $\text{S}_2\text{O}_8^{2-}$, P2S- $\text{S}_2\text{O}_8^{2-}$, 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 compensated by the sulfonate groups is proportional to the total amount of PANI covering the surface of the membrane. Moreover,

Table 5.3 shows that the $S_{\text{PANI}^+}/S_{\text{total}}$ 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 confirms 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

5.4.3. 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 solvent 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 5.4 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 (Table 5.2). 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 5.2 and Table 5.4) do not indicate any degradation of the sulfonic acid groups in the CMX membrane.

Table 5.4. Elemental analysis and physical properties of the bulk membranes.

| | Elemental analysis [*] | | IEC mmol/g | H ₂ O wt % | λ mol _{H₂O} / mol _{SO₃⁻} | Zn ²⁺ leakage % | R Ωcm^2 | σ mS/cm |
|---|---------------------------------|-----------|---------------|--------------------------|---|----------------------------------|--------------------------|-------------------|
| | wt % N | wt % S | | | | | | |
| Bare CMX | 0.61 ± 0.07 | 5.1 ± 0.6 | 1.61 | 22.5 | 10 | 7.9 | 0.226 | 75 |
| P1S-S ₂ O ₈ ²⁻ | 0.72 ± 0.04 | 5.1 ± 0.1 | 1.60 | 22.1 | 9.9 | 0.1 | 0.370 | 46 |
| P1S-Fe ³⁺ | 0.77 ± 0.02 | 5.0 ± 0.1 | 1.59 | 21.7 | 9.7 | 7.4 | 0.246 | 69 |
| P1S-H ₂ O ₂ | 0.78 ± 0.04 | 5.1 ± 0.1 | 1.62 | 22.4 | 9.9 | 7.5 | | |
| P2S-S ₂ O ₈ ²⁻ | 0.76 ± 0.03 | 5.0 ± 0.2 | 1.57 | 21.6 | 9.8 | < 0.1 | 0.359 | 47 |
| P2S-Fe ³⁺ | 0.87 ± 0.04 | 4.8 ± 0.4 | 1.53 | 21.6 | 10.0 | 0.1 | 0.447 | 38 |
| P2S-H ₂ O ₂ | 0.76 ± 0.06 | 5.1 ± 0.4 | 1.63 | 22.3 | 9.8 | 7.8 | | |

^{*}The values given are an average of 5 replicas.

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 SO₃⁻ 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 5.1). 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 5.4 shows that although very little changes in IEC are observed, their values are consistent with the data obtained by elemental analysis given in Table 5.4. 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 indicate 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ instead of 0.3 M. The PANI layer was visually much darker than the PANI layers obtained here. Table 5.4 also shows that no significant variation in the quantity of water absorbed is observed suggesting that no swelling or shrinking occurs after modification.

5.4.4. *Transport Properties of the Membranes*

To evaluate the influence of the PANI layer on the permselectivity properties of the modified membranes, electro dialysis 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 5.4, it appears that the following membranes block the transport of bivalent cations: P1S-S₂O₈²⁻ (0.1%), P2S-S₂O₈²⁻ (< 0.1%), and P2S-Fe³⁺ (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-Fe³⁺ contains about the same amount of PANI as P1S-S₂O₈²⁻ (Table 5.4) but leads to a high metal leakage (Table 5.4). This confirms the hypotheses proposed in a previous work.¹³

For the membranes with a PANI layer blocking the transport of Zn²⁺ ions, it is important to ensure that these membranes do not lead to a significant increase in resistance during electro dialysis which would lead to a loss in ionic conductivity. Therefore, conductivity measurements were performed in 0.5 M H₂SO₄. Table 5.4 indicates that a very small decrease in ionic conductivity (σ) is observed when membranes contain a PANI layer but σ still remains in the same order of magnitude. Although imine and amine groups from the PANI chains can conduct protons,²⁶ the decrease in σ could be because these functional groups are not as good of a 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 5.3, imply that the number of free SO₃⁻, 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 σ values can be contrasted with the S 2*p* XPS data (Table 5.3) 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 S 2*p* 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 of about 10 nm) whereas IEC is related to the amount of free -SO₃⁻ 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.

5.5. DISCUSSION

5.5.1. 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 potentials and being either neutral (H_2O_2), positively (Fe^{3+}), or negatively charged ions ($\text{S}_2\text{O}_8^{2-}$) were chosen. The standard reduction potential for these oxidants, given in Table 5.5, can be compared to the relative quantity of polyaniline found at the surface and within the membrane (Tables 5.2 and 5.3).

Table 5.5. Standard reduction potentials for various oxidants used in the chemical polymerization of aniline.

| Half-reaction | E^0 (V/NHE) ²⁷ |
|--|-----------------------------|
| $\text{S}_2\text{O}_8^{2-} + 2 e^- \rightarrow 2 \text{SO}_4^{2-}$ | 1.94 |
| $\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 e^- \rightarrow 2 \text{H}_2\text{O}$ | 1.78 |
| $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ | 0.77 |

First, XPS data indicate that the strongest oxidant, ammonium peroxodisulfate ($E^0 = 1.94$ 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 ($E^0 = 1.78$ 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.²⁸ 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 media in our study since degradation of the polyaniline chains occurs rapidly upon hydrolysis in very acidic solutions.^{13, 29} For membranes prepared with Fe^{3+} , the weakest oxidant used ($E^0 = 0.77 \text{ V}$), 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 $\text{P2S-S}_2\text{O}_8^{2-}$.

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: $\text{P1S-S}_2\text{O}_8^{2-} < \text{P1S-Fe}^{3+} \cong \text{P1S-H}_2\text{O}_2$, whereas for the membranes prepared using the two-step method, we have: $\text{P2S-S}_2\text{O}_8^{2-} \cong \text{P2S-H}_2\text{O}_2 < \text{P2S-Fe}^{3+}$. 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 ($E^0 = 1.09 \text{ V}$). From a thermodynamic point of view, this latter oxidant should lead to a membrane having a PANI content lying between the membranes prepared with $\text{S}_2\text{O}_8^{2-}$ 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.³⁰ for the polymerization of aniline in solution.

5.5.2. *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 ($-\text{SO}_3^-$). In fact, XPS results given in Figures 5.3 and 5.4 reveal that in the case of the one-step modification method, only membranes prepared with a negatively charged oxidant, $\text{S}_2\text{O}_8^{2-}$, 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, $\text{C}_6\text{H}_5\text{-NH}_3^+$, 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 5.3 and 5.4) 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 5.3) 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 5.1).

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 $-\text{SO}_3^-$ groups and the $\text{C}_6\text{H}_5\text{-NH}_3^+$ ions. Therefore, polymerization of aniline can occur both at the surface and within the bulk of the membrane and in fact, elemental analysis (Table 5.3) shows that Fe^{3+} leads to a larger 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 $\text{P2S-S}_2\text{O}_8^{2-}$ 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 towards bivalent cations.

5.5.3. *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 5.5 suggests that both P1S-S₂O₈²⁻ and P2S-S₂O₈²⁻ 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-Fe³⁺ 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-Fe³⁺ 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 5.3) is higher than for P2S-S₂O₈²⁻ which in turn, has a larger amount of PANI at the surface of the membrane (Table 5.3 and Figure 5.3b). When comparing the electro dialysis 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 5.5 shows that only the membranes having a PANI coating at the surface of the membrane, that is, membranes prepared using ammonium peroxydisulfate 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 Zn²⁺ during electro dialysis in acidic media. Moreover, the membranes prepared with KIO₃ (24 h reaction time) (not shown) led to a Zn²⁺ 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.

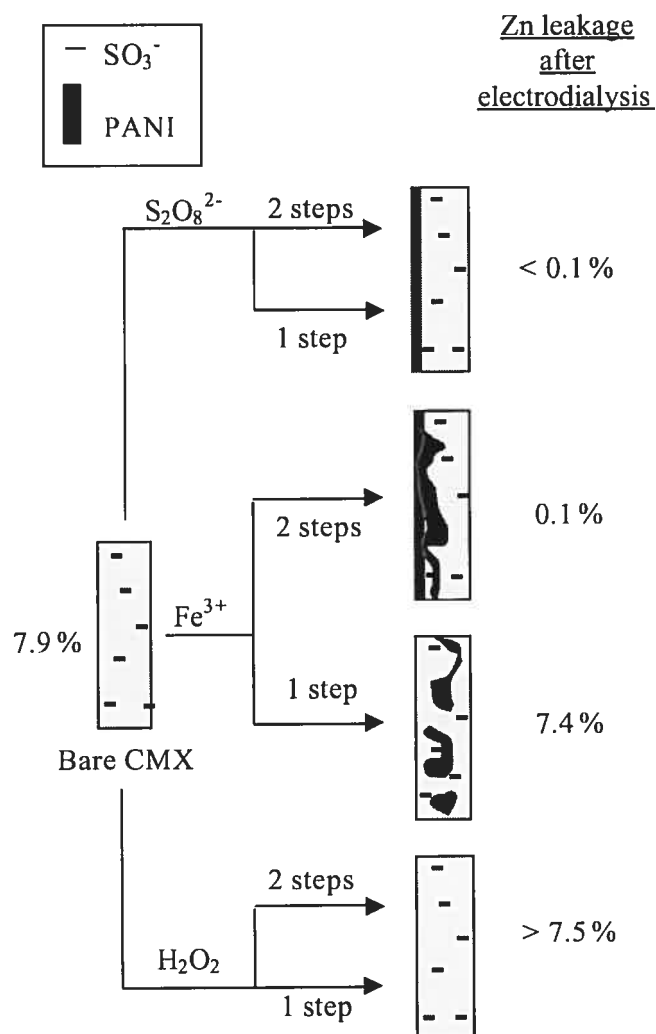


Figure 5.5. Schematic representing different polymerization sites of aniline obtained with the different oxidants studied in relation with the Zn^{2+} leakage obtained after electro dialysis in 0.5 M H_2SO_4 .

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, electrodiályses were carried out for the P1S-S₂O₈²⁻ and P1S-Fe³⁺ membranes with the surface exposed to the oxidant facing the catholyte. For the P1S-Fe³⁺ membrane, no change in Zn²⁺ 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-S₂O₈²⁻ membrane, a higher Zn²⁺ leakage (5.3 vs 0.1%) was obtained when placing the PANI layer facing the catholyte.

The variation of potential during electrodiálisis (Figure 5.6) was also different. Figure 5.6b shows that during the first 15 min of electrodiálisis, 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 Zn²⁺ 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 Zn²⁺ 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 SO₃⁻ 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 SO₃⁻ groups of the membrane. Hence, when the Zn²⁺ concentration within the membrane is high enough, transport of Zn²⁺ 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 Zn²⁺. Thus, the electrodiálisis 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 Zn²⁺ 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+} .

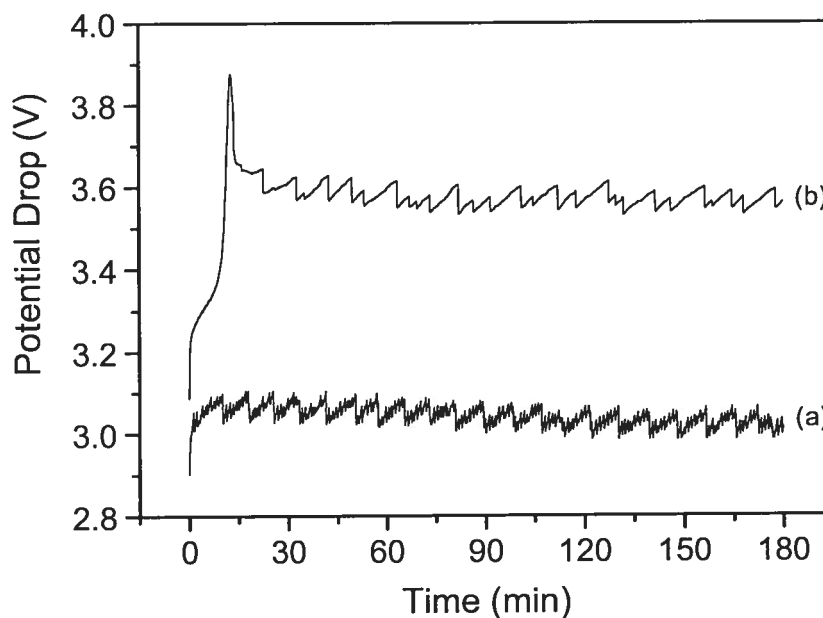


Figure 5.6. Potential drop versus time curves obtained during electro dialysis of 1500 ppm Zn^{2+} in 0.5 M H_2SO_4 using the $\text{P1S-S}_2\text{O}_8^{2-}$ membrane with the surface exposed to the oxidant facing the anolyte (a) and facing the catholyte (b).

5.6. 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 in order to block the transport of Zn^{2+} while maintaining the transport of H^+ through the membrane during electro dialysis, 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.

5.7. ACKNOWLEDGMENTS

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Chapitre 6

*Stabilité thermique et chimique des
membranes composites
poly(styrène sulfonate)/polyaniline*

6.1. INTRODUCTION

Dans les chapitres précédents, il a été démontré que la présence de la polyaniline à la surface des membranes Neosepta CMX permet un blocage du transport des ions Zn^{2+} et Cu^{2+} lors des électrodialyses en milieu acide. Par ailleurs, il suffit qu'une couche très mince de PANI soit présente à la surface de la membrane pour rendre la membrane composite CMX-PANI permselective aux protons.

Le choix de la polyaniline pour la modification des membranes échangeuses de cations est justifié non seulement par la facilité avec laquelle il est possible de polymériser chimiquement l'aniline mais également par sa stabilité chimique et thermique. En fait, des chercheurs ont déjà démontré que la polyaniline, sous sa forme émeraude, est stable à l'air et en milieu aqueux (pH 1).¹⁻³

Par ailleurs, l'un des obstacles majeurs dans le développement et l'utilisation des membranes échangeuses ioniques modifiées est la stabilité de ces dernières lors des électrodialyses de longue durée. Entre autres, Bailey et al.⁴ ont démontré que la membrane Neosepta CMS, une membrane permselective aux cations monovalents, perdait complètement sa sélectivité après 300 h d'électrodialyse. Leurs résultats SEM démontrent également qu'il y a délamination de la couche de surface de la membrane CMS.

Par conséquent, il serait pertinent d'évaluer la stabilité de notre membrane composite CMX-PANI face aux électrodialyses. Ainsi, ce chapitre présente les résultats obtenus lors des électrodialyses de longue durée et lors des électrodialyses effectuées à répétition. Une brève discussion sur la stabilité des membranes CMX-PANI en solution est également présentée à la fin de ce chapitre. La première section des résultats présente la stabilité thermique de la membrane composite CMX-PANI évaluée par analyse thermogravimétrique.

6.2. PARTIE EXPÉRIMENTALE

La membrane composite choisie pour les expériences de stabilité est la CMX modifiée en une étape avec le persulfate d'ammonium (0.3 M) caractérisée dans le chapitre 5 et nommée CMX P1S-S₂O₈²⁻. La méthode de modification de la membrane composite CMX-PANI est décrite aux sections 5.3.2 et 5.4.1.

L'analyse thermogravimétrique a été effectuée avec des échantillons mouillés et préalablement conditionnés dans 1 M HCl. Les thermogrammes ont été enregistrés avec un instrument TGA de modèle Seiko Exstar 6200 TG/DTA sous air comprimé avec une rampe de température de 10°C/min.

La procédure utilisée des électrodialyses est décrite à la section 5.3.8. Les électrodialyses ont toutes été effectuées avec la surface de la membrane modifiée exposée au compartiment anodique, contenant initialement les ions Zn²⁺.

L'image SEM a été enregistrée avec un microscope électronique à balayage Hitachi modèle S-2300 à un angle de 60° par rapport à la surface.

6.3. RÉSULTATS ET DISCUSSION

6.3.1. Stabilité thermique

La Figure 6.1 montre les courbes obtenues par analyse thermogravimétrique pour les membranes CMX non-modifiée et CMX P1S-S₂O₈²⁻. Tout d'abord, la Figure 6.1 montre que la décomposition thermique de la CMX est divisée en quatre étapes qui consistent en: i) l'évaporation de l'eau entre 25 et 100°C; ii) l'élimination de HCl entre 200 et 375°C provenant du poly(chlorure de vinyle),⁵ le support de la membrane CMX; iii) la décomposition des groupements sulfonates entre 390 et 425°C⁶ et iv) la décomposition des chaînes de carbone entre 495 et 625°C. Après modification de la membrane CMX avec la polyaniline, aucun changement majeur n'est observé. La polyaniline ne semble donc pas changer la stabilité thermique de la membrane.

En outre, la Figure 6.1 montre qu'il n'est pas possible de discerner la dégradation thermique de la polyaniline, généralement observée entre environ 380 et 600°C en présence d'air pour la forme émeraldine.^{7, 8} La faible quantité de polyaniline présente dans la membrane composite (moins de 1% en masse)⁹ et la décomposition des groupements sulfonates et des chaînes de carbone dans la même région de température empêcherait la détection de la décomposition de la polyaniline.

Seule une légère différence en pourcentage d'eau est observée entre la CMX (19%) et la CMX P1S-S₂O₈²⁻ (16%). Il est à noter que ces valeurs de pourcentage d'eau sont plus faibles que les valeurs correspondantes obtenues par différence de masse, données dans le Tableau 5.4 (section 5.4.3) qui sont de 23% pour la CMX et 22% pour la CMX P1S-S₂O₈²⁻. Cette différence peut être attribuable à l'évaporation de l'eau durant la préparation des échantillons pour l'analyse thermogravimétrique, car ces derniers avaient une masse initiale d'environ 5 mg.

6.3.2. Stabilité après électrodialyses à répétition

Une série d'électrodialyses de 3 h à 50 mA/cm² ont été réalisées avec une membrane CMX P1S-S₂O₈²⁻. Entre chacune des électrodialyses, les membranes ont été trempées dans une solution de 1 M H₂SO₄ pour enlever toutes traces d'ions Zn²⁺. La Figure 6.2 montre que le taux de fuite en zinc augmente très peu en fonction du nombre total d'heures d'utilisation en électrodialyse. Après 15 électrodialyses, le taux de fuite en Zn²⁺ demeure inférieure à 0.1 %, une valeur considérée comme étant dans la marge d'erreur expérimentale. Par ailleurs, ce taux de fuite peut être associé à un nombre de transport défini comme étant la fraction du courant circulant dans la cellule transporté par l'ion *i*.

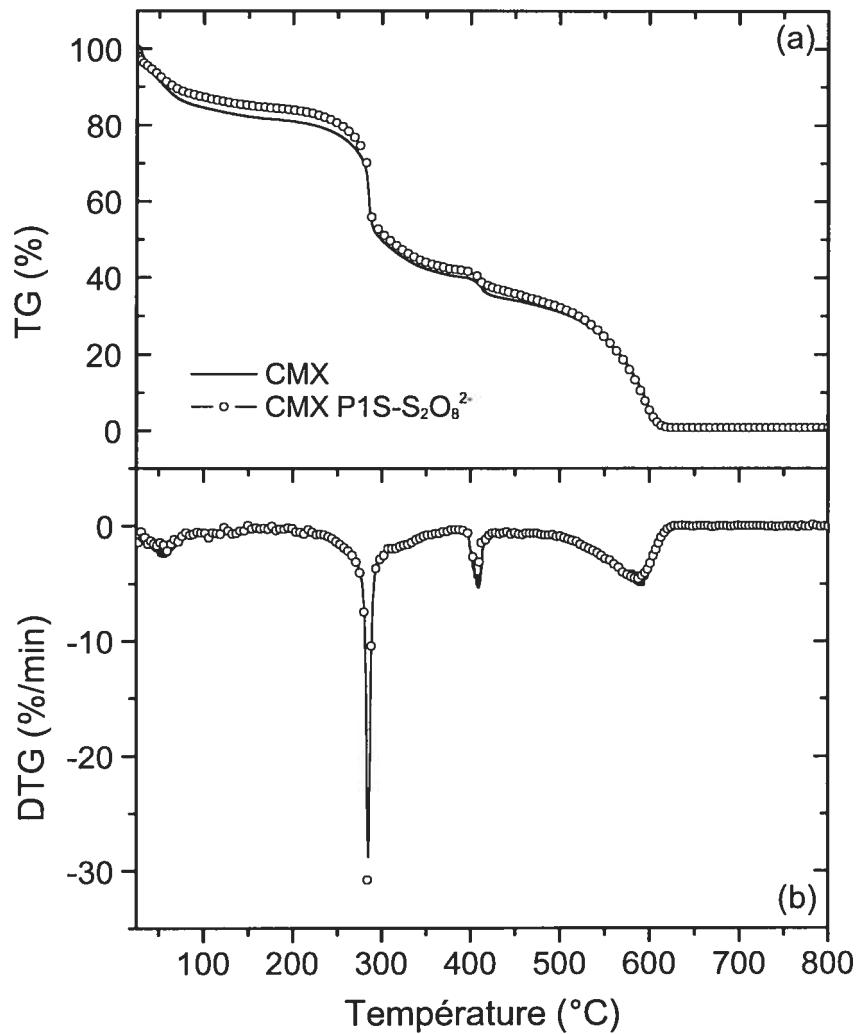


Figure 6.1. Analyse TGA des membranes CMX et CMX P1S-S₂O₈²⁻ effectuée sous air. Les courbes de perte en masse sont représentées en (a) et la dérivée correspondante de ces courbes en (b).

Le nombre de transport, t_i , peut être calculée par l'équation suivante¹⁰:

$$t_i = \frac{1000z_iJ_iF}{j} \quad (6.1)$$

où z_i est la valence de l'espèce i , J_i , le flux de l'espèce i (mol/cm²•s), F , la constante de Faraday (96485 C par mol d'ions) et j , la densité de courant (mA/cm²). Le flux J_i est déterminé par:

$$J_i = \frac{V_c(C_i^S - C_i^0)}{A \cdot T^S} \quad (6.2)$$

où V_c est le volume de la solution cathodique (L), C_i^S , la concentration de l'espèce i dans le compartiment cathodique au temps T^S (mol/L), C_i^0 , la concentration initiale de i (mol/L), A , la surface apparente de la membrane (cm²) et T^S , le temps d'électrodialyse (s).

Ainsi, un taux de fuite de 0.07%, obtenu après 15 électrodialyses, correspond à un nombre de transport, $t_{Zn^{2+}}$, de 0.0002, une valeur inférieure à celle donnée dans la littérature pour les membranes commerciales de type Neosepta CMS, qui est d'environ 0.005 pour le même temps d'électrodialyse.¹⁰ La membrane composite CMX-PANI semble donc maintenir sa sélectivité face à une utilisation répétée en électrodialyse.

6.3.3. Stabilité en fonction du temps d'électrodialyse

La Figure 6.3 illustre le taux de fuite du Zn^{2+} en fonction du temps d'électrodialyse. Les résultats démontrent que la membrane CMX P1S-S₂O₈²⁻ perd sa sélectivité aux protons assez rapidement. Après 12 h d'électrodialyse, un taux de fuite en Zn^{2+} supérieure à 0.1% est obtenu et après 48 h d'électrodialyse, le taux de fuite est de 2.2%. Cette valeur est toutefois inférieure à celle obtenue avec la membrane CMX non modifiée (7.9%, voir Tableau 5.4 dans le chapitre précédent).

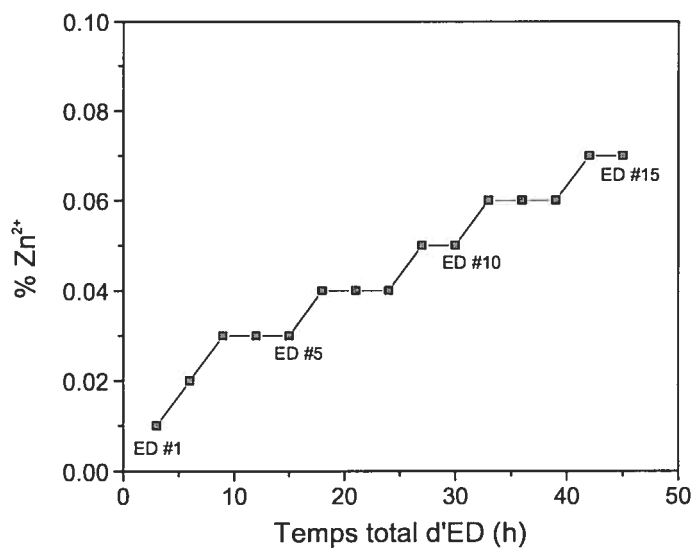


Figure 6.2. Taux de fuite en Zn^{2+} obtenu avec la membrane CMX P1S-S₂O₈²⁻ après plusieurs électrodialyses de 3 h à 50 mA/cm² d'une solution contenant 1.5 g/L de Zn^{2+} dans 0.5 M H₂SO₄.

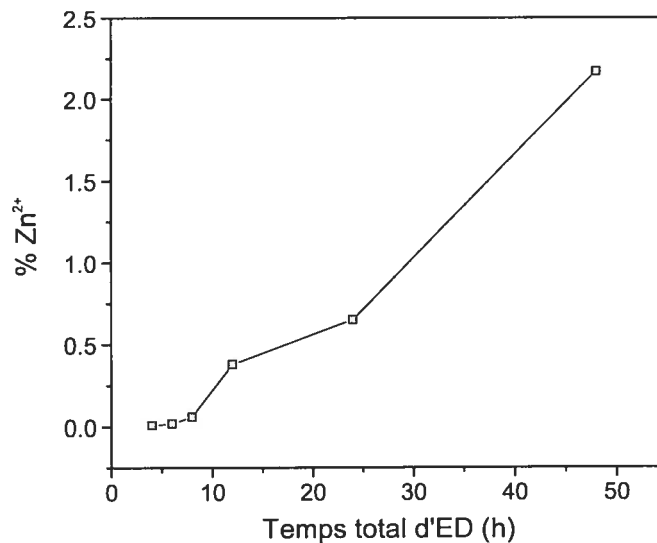


Figure 6.3. Taux de fuite en Zn^{2+} obtenu avec la membrane CMX P1S-S₂O₈²⁻ après une électrodialyse effectuée à 50 mA/cm² en milieu 0.5 M H₂SO₄ en fonction du temps d'électrodialyse. Une nouvelle membrane est utilisée pour chacune de ces électrodialyses.

La principale différence entre les résultats présentés à la Figure 6.3 et la Figure 6.2 est l'étape de lavage de la membrane après trois heures d'électrodialyse dans ce dernier cas. La corrélation entre résultats semble indiquer que la perte de sélectivité observée à des temps d'électrodialyses supérieures à 12 h n'est pas associée à la perte de la couche de PANI. La surface de la membrane composite utilisée pour l'électrodialyse de 48 h a été observée par microscopie électronique à balayage. La Figure 6.4 montre que la couche de PANI est demeurée intacte et ce, sur toute la surface sondée par SEM.

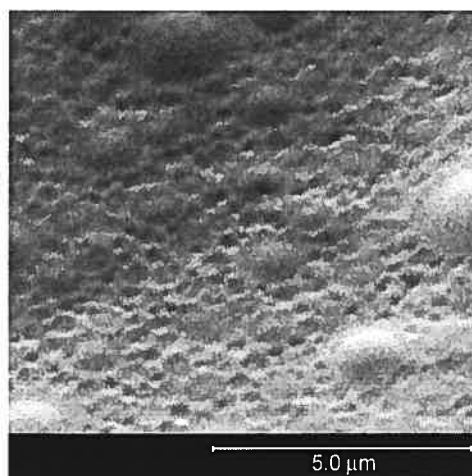


Figure 6.4. Image SEM de la surface de la membrane CMX P1S-S₂O₈²⁻ après avoir été utilisée pour une électrodialyse de 48 h.

De plus, après une période de trempage dans 1 M H₂SO₄ de plus de 24 h, une électrodialyse de 3 h a été effectuée avec la membrane utilisée pour l'ED de 48 h. Le taux de fuite obtenue suite à cette électrodialyse est de 0.1%, ce qui confirme que la membrane est demeurée intacte.

Donc, la perte de sélectivité de la membrane composite CMX P1S-S₂O₈²⁻ serait possiblement due à une accumulation d'ions Zn²⁺ à la surface ou à l'intérieur membrane. Par ailleurs, l'accumulation de cations bivalents à l'intérieur de la

membrane a été observée durant les électrodialyses de 3 h effectuées avec une membrane CMX P1S-S₂O₈²⁻ et la surface modifiée orientée vers la solution cathodique (section 5.5.3). Cette perte de sélectivité après une électrodialyse de longue durée a également été observée avec les membranes commerciales Neosepta CMS. Boucher et al. expliquent ce phénomène par l'adsorption de cations bivalents à la surface de la membrane.¹⁰

6.3.4. Stabilité en solution

Comme il a été mentionné précédemment, Hobaica a démontré que la polyaniline, sous sa forme émeraude, est stable en milieu acide (pH 1) et à l'air.¹ Cependant, d'autres chercheurs ont suggéré que la polyaniline pouvait se dégrader après entreposage dans une solution de 1 M HCl.¹¹ Par ailleurs, la PANI est soluble dans l'acide sulfurique concentré ce qui laisse croire que la PANI pourrait éventuellement être dégradée par hydrolyse lorsque conservée dans une solution aqueuse suffisamment concentrée en acide.

Afin d'évaluer la stabilité en solution des membranes composites CMX-PANI, des membranes CMX P1S-S₂O₈²⁻ ont été entreposées dans des solutions acides relativement concentrées pendant plusieurs mois. Les résultats indiquent qu'après plus de 4 mois de trempage dans une solution de 1 M HCl, la membrane maintient un taux de fuite faible en Zn²⁺ (< 0.1%) pour une électrodialyse de 3 h. De même, la membrane CMX P1S-S₂O₈²⁻ garde ses propriétés de permselectivité pendant au moins 1 mois dans 1 M H₂SO₄. De ce fait, les membranes CMX P1S-S₂O₈²⁻ semblent être chimiquement stables pendant plusieurs semaines dans les solutions de 1 M HCl et 1 M H₂SO₄.

6.4. CONCLUSION

En résumé, les résultats de ce chapitre semblent démontrer que la membrane composite CMX-PANI possède une bonne stabilité thermique, chimique et

mécanique. En effet, les mesures d'analyse thermogravimétrique montrent que la présence de la PANI n'a pas d'effet sur la stabilité thermique de la membrane. Les essais d'électrodialyses à répétition et d'électrodialyses de longue durée suggèrent que la couche de PANI polymérisée à la surface de la membrane CMX ne se détache pas de la membrane. Ceci peut être expliqué par le fait que la couche de PANI est polymérisée au sein de la membrane et que cette méthode permet de former une couche de PANI partiellement entrelacée dans la membrane CMX. Par ailleurs, les résultats de stabilité de la membrane en électrodialyse sont comparables et même meilleurs que ceux obtenus avec la membrane commerciale CMS. Par contre, la membrane subit une légère perte de permselectivité lors des électrodialyses de longue durée due à l'augmentation de la concentration des cations métalliques adsorbés dans la membrane composite.

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Chapitre 7

Characterization and Transport Properties of Nafion/Polyaniline Composite Membranes

Sophie Tan and Daniel Bélanger

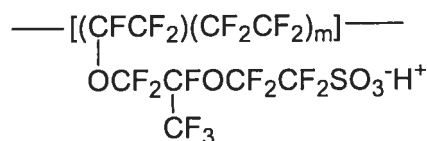
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7.1. ABSTRACT

Nafion membranes were modified by chemical polymerization of aniline using ammonium peroxodisulfate as the oxidant. The Nafion-polyaniline composite membranes were extensively characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), infrared (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and ion exchange capacity measurements. The transport properties were also evaluated by conductivity and electro dialysis measurements. The data shows that when a high oxidant concentration (1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$) is used, polyaniline is mostly formed at the surface of the Nafion membrane with a higher proportion of oligomers. On the contrary, when 0.1 M oxidant is used, polyaniline is mostly formed inside the ionic domains of Nafion, blocking the pathway to ion transport and thus, reducing the transport of Zn^{2+} as well as the transport of H^+ . These data were also compared to the data obtained with poly(styrene sulfonate)-PANI composite membranes.

7.2. INTRODUCTION

Perfluorinated ionomer based polymers have been studied since late 1970s with the commercialization of Nafion membranes from DuPont. These membranes were first used in the chlor-alkali industry for electro dialysis processes. The structure of Nafion is illustrated below. It is mainly composed of a poly(tetrafluoroethylene) (PTFE) backbone with side-chains containing ether groups and a sulfonic acid unit at its end.



where $m = 6.5$ for Nafion 117
with an equivalent weight (EW) of 1100

Scheme 1. Structure of Nafion.

Nowadays, perfluorinated membranes are extensively studied for their applications in fuel cells, particularly, for direct methanol fuel cells. To date, Nafion is still the most performing cation exchange membrane due to its high chemical and mechanical stability as well as its good proton conductivity.¹ However, some progress is still needed in order to enhance the membranes performance in terms of permselectivity, water management and stability at high temperatures. For this reason, researchers have synthesized new polymeric membranes derived from the perfluorosulfonic acid structure.^{2,3} Others have studied the modification of Nafion membranes using inorganic fillers such as SiO₂,^{4,5} mordenite,⁶ inorganic acids^{7,8} a polymer coating and/or filler such as poly(vinyl alcohol),⁹ poly(1-vinylimidazole),¹⁰ poly(vinylidene fluoride).¹¹ Nafion has also been modified with conducting polymers such as poly(pyrrole)¹²⁻¹⁶ and poly(aniline) (PANI)¹⁷ to reduce the methanol crossover in direct methanol fuel cell applications. Sata et al.¹⁸ have briefly mentioned about the use of perfluorocarbon sulfonic acid modified with polypyrrole for electro dialysis applications. Nevertheless, very few teams have studied the Nafion-PANI composite membranes. Nafion-PANI composites have been studied mostly for electrode modifications in order to mix the electronic conductivity of PANI and the ionic conductivity of Nafion.¹⁹⁻²³

Prior to this work, we have demonstrated the possibility of improving the permselectivity of poly(styrene sulfonic acid) membranes for the transport of protons against bivalent cations (Zn²⁺ and Cu²⁺) by modifying these membranes with a thin layer of polyaniline.^{24,25} It was also shown that the permselectivity behavior was linked to the location of the PANI layer within the membrane matrix.²⁶

The aim of this work is to study the modification of Nafion 117 membranes by in-situ chemical polymerization of aniline. More specifically, the Nafion-PANI membrane will be extensively characterized using several techniques in order to understand how the microstructure of this composite membrane affects its transport properties in electro dialysis applications.

7.3. EXPERIMENTAL SECTION

7.3.1. Materials and Chemicals

HCl (EMD), H₂SO₄ (EMD), NaCl (BDH), (NH₄)₂S₂O₈ (BDH), and ZnSO₄·7 H₂O (Anachemia) were of ACS reagent grade and used as received. Aniline (Acros) was distilled twice prior to use. Millipore water (18 MΩ·cm obtained from a Sybron/Barnstead Nanopure system) was used for the preparation of all solutions. The perfluorosulfonate cation-exchange membrane used in this study was the Nafion[®] 117 (DuPont). The membrane was pretreated by boiling in H₂O₂ (3% v/v), H₂O, H₂SO₄ (0.5 M) and H₂O for 1 h and stored in 1 M HCl.

7.3.2. Membrane Modification with Polyaniline

The Nafion membranes were conditioned in 1 M HCl for more than 24 h prior to modification. The modification was carried out in two steps at room temperature in a Teflon two-compartment cell (surface modified: 9.6 cm²). The first step consisted of exchanging the protons in the membrane with protonated aniline, that is, anilinium ions, by adding, in one compartment, 40 mL of 1 M aniline solution in 1 M HCl, and water in the second compartment. After rinsing with water, the aniline solution was replaced by 40 mL of 1 or 0.1 M (NH₄)₂S₂O₈ solution. This second step polymerizes the anilinium species exchange within the membrane. The two-step method allows modification on a single face of the membrane. The modified membranes were stored either in 1 M HCl or 1 M H₂SO₄ solutions. The membrane identification is as follows: Naf PX-Y-Z where P stands for polyaniline, X represents the time (h) used in the exchange of anilinium ions, Y is the reaction time (h), and Z is the concentration (M) of the oxidant.

7.3.3. Instrumental Characterization

For all instrumental techniques, membranes were conditioned in 1 M HCl. When required, membranes were dried under vacuum for at least 36 h at room temperature in the presence of P₂O₅.

Atomic force microscopy (AFM) images were recorded in the tapping mode using a Nanoscope III Dimension 3100 AFM instrument (Digital Instruments) with an etched silicon aluminum coated tip. Samples were only partially dried with a nitrogen flow to remove surface water. Scanning electron microscopy (SEM) micrographs were taken using a Hitachi model S-4300E/N scanning electron microscope with dried samples. SEM samples were sputtered with gold to reduce charging effects during measurements.

The Fourier transform infrared (FTIR) spectra were recorded using a Thermo-Nicolet Nexus 870 spectrometer equipped with a mercury cadmium telluride (MCTA) detector and a ZnSe attenuated total reflection (ATR) platform. The spectra shown are obtained with dried samples using 128 scans at a resolution of 4 cm⁻¹.

XPS analyses were performed using a VG Escalab 220i-XL system equipped with a hemispherical analyzer and an Al anode (K α 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 C 1s 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. The surface atomic composition was calculated using the high resolution spectra and the appropriate relative sensitivity factors: C 1s (1.00), F 1s (4.43), 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).

Thermogravimetric (TGA) and differential scanning calorimetry (DSC) measurements were done with wet samples from which excess water was removed by wiping the membranes using a filter paper. The TGA thermograms were recorded using a Seiko Exstar 6200 TG/DTA and the DSC thermograms, with a TA Instrument 2910 DSC equipped with a liquid nitrogen cooling accessory (LNCA).

7.3.4. Ion-Exchange Capacity (IEC)

All membranes were washed and stabilized in 1 M HCl, H₂O and 1 M NaCl alternatively for 1 h in each solution during 3 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 P₂O₅ 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).

7.3.5. Water Content

The membranes were washed, stabilized, and conditioned in 1 M HCl as for IEC measurements. After removing excess chloride by immersion in water and rinsing with water, the membranes were blot dried with a filter paper and weighed immediately. Then, the membranes were dried (under vacuum at room temperature for at least 36 h over P₂O₅) and weighed again. The % H₂O was determined according to the following equation:

$$\%H_2O = \frac{m_{\text{wet membrane}} - m_{\text{dry membrane}}}{m_{\text{wet membrane}}} \times 100 \quad (7.1)$$

where *m* is the mass (g).

7.3.6. Electrodialysis

Electrodialyses were performed in a two-compartment cell containing, in the anodic compartment, 150 mL of 1.5 g/L Zn²⁺ in 0.5 M H₂SO₄ and in the cathodic compartment, 33 mL of 0.5 M H₂SO₄. 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 100 mA/cm^2 was applied between two platinum plates (surface area: $\sim 7.5 \text{ cm}^2$) for 3 h using a M273 potentiostat/galvanostat (EG & G Princeton Applied Research). The electro dialysis was carried out 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 where m is the mass (g):

$$\% \text{Zn}^{2+} \text{ leakage} = \frac{m_{\text{Zn}^{2+}}(\text{catholyte})}{m_{\text{Zn}^{2+}}(\text{catholyte}) + m_{\text{Zn}^{2+}}(\text{anolyte})} \times 100 \quad (7.2)$$

7.3.7. Conductivity Measurements

Measurements were carried out at room temperature (23 ± 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 $1 \mu\text{A/s}$ and the open-circuit voltage was measured between two Ag/AgCl (3 M KCl) reference electrodes placed on each side of the membrane at a distance of 4 mm from its surface. The instrument used to apply the current and 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 using the membrane thickness measured with a Mitutoyo model 227-211 micrometer. The solution ionic resistance was measured using the same setup, and its value was subtracted from the resistance values measured to calculate the membrane resistance and conductivity values.

7.4. RESULTS

7.4.1. Chemical Polymerization of Aniline on Nafion

In this work, polymerization was carried out in a two-compartment cell to favor polymerization on a single face of the membrane. In fact, a minimal quantity of PANI is desired on the membrane in order to block transport of bivalent cations and, in the meantime, maintaining good ionic conductivity. After exchanging the Nafion counterions (H^+) with anilinium ions (protonated aniline), the cell was rinsed several times with water before replacing the aniline solution by the peroxodisulfate ammonium solution $((NH_4)_2S_2O_8)$, the oxidant. Concentrations of 0.1 and 1.0 M oxidant were studied. When using the 1 M oxidant solution, polymerization takes place quite rapidly but a visually homogeneous and dark PANI layer is obtained only after 1 h of polymerization (Naf P1-1-1). Over 1 h of polymerization, the PANI layer was visually similar but the blocking behavior of the membrane for Zn^{2+} is lost, most likely due to the degradation of PANI.²⁴ With 0.1 M $(NH_4)_2S_2O_8$, a transparent but homogeneous PANI layer is obtained after 1 h of oxidation. Yet, only the membrane prepared with a 2 h oxidation time (Naf P1-2-0.1) yielded in a good blocking behavior toward Zn^{2+} ions (see below). Therefore, only the Naf P1-1-1 and Naf P1-2-0.1 were characterized and presented in this article. Visually, both composite membranes exhibit the same dark blue color. However, it should be mentioned that after 1 h of oxidation using 1 M $(NH_4)_2S_2O_8$, a yellow-brown precipitate is found in the water compartment, opposite to the compartment containing the oxidant. This precipitate has the characteristic color of benzoquinone, the degradation product of PANI following hydrolysis.^{24,27,28} Also, after storage of Naf P1-1-1 in 1 M HCl or H_2SO_4 for over 24 h, a pink color appears on the unmodified surface of the membrane around the modified area. At longer storage times, the aqueous solution also becomes pink. The pink color was not observed in the case of Naf P1-2-0.1 even over two months of storage in acid solutions (1 M HCl). These observations suggests that the use of 1 M $(NH_4)_2S_2O_8$ can lead to

the presence of oligomers on the Naf P1-1-1 membrane which can diffuse through the membrane.

7.4.2. SEM and AFM

Figure 7.1, parts a and b, present the SEM surface micrographs of the bare Nafion and Naf P1-1-1 membranes. After modification, a change in surface topography is observable. The PANI coating seems to be heterogeneous, displaying some aggregates along with some fibril-like structures. However, one should be very careful in attributing the surface features solely to the presence of PANI, particularly for images obtained by SEM at high magnification factors. It was observed that the Nafion surface topography tends to change during image acquisition due to burning and degradation of the surface and this, even with a gold coating added to minimize surface charging effects. For example, Figure 7.1a shows some cracks at the surface of Nafion which appear during image acquisition. These cracks are formed most likely due to water removal from the surface and burning effects. The formation of holes on Nafion was also observed during irradiation of a surface with Ga^+ ions using the focused ion-beam technique (known as FIB).²⁹ Nevertheless, some coating is apparent at the surface of the modified membranes.

The membrane topography can also be monitored by atomic force microscopy. The advantage of AFM (tapping mode) over SEM is that AFM can probe the surface of the membrane without using a radiation source that can burn the surface and without adding a gold layer which could slightly alter the topography of the membrane. In addition, AFM imaging can be performed in a partially dried state whereas the conventional SEM technique used in this work requires drier samples. Drying can also introduce changes in the surface morphology of the polymers, as mentioned above.

AFM images of the unmodified and modified Nafion (Naf P1-1-1) are presented in Figure 7.1, parts c and d. Comparison of Figure 7.1, parts c and d, depicts some similar features such as the presence of linear and particulate structures. The linear structure found on the Nafion surface is most likely caused by the

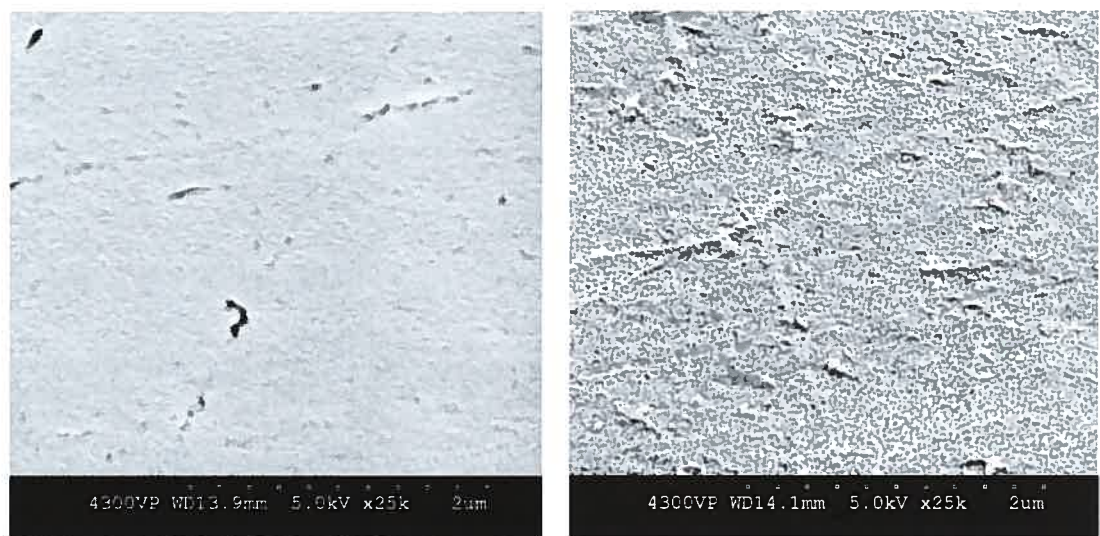
extrusion procedure used in the preparation of the Nafion commercial membrane.^{30,31} Despite the similarities found on the surface of both membranes, Figure 7.1d shows that the modification enhances these defects at the surface of Nafion suggesting that polymerization occurs primarily at surface imperfections of the membranes. However, the density of polyaniline fibrils seems to be larger than the density of linear surface imperfections, but the entire surface is not covered by PANI. Interestingly, the fibril-like structure of PANI was also observed by Wen and Kocherginsky³² for polyaniline membranes doped with 1 M HCl such as in the case of the membranes presented in Figure 7.1.

The differences observed between Figure 7.1, parts b and d, can be attributed to the drying state of the membrane as well as the fact that SEM can alter the surface of the Nafion membrane after irradiation. It should also be noted that SEM probes a few micrometers depth and the image acquired is actually an image of the first few micrometers of the membrane. In contrast, the AFM technique probes the surface with a depth in the order of nanometers (100 nm in this case). The PANI fibril-like structure is possibly present only at the surface of the membrane.

7.4.3. FTIR-ATR Spectroscopy

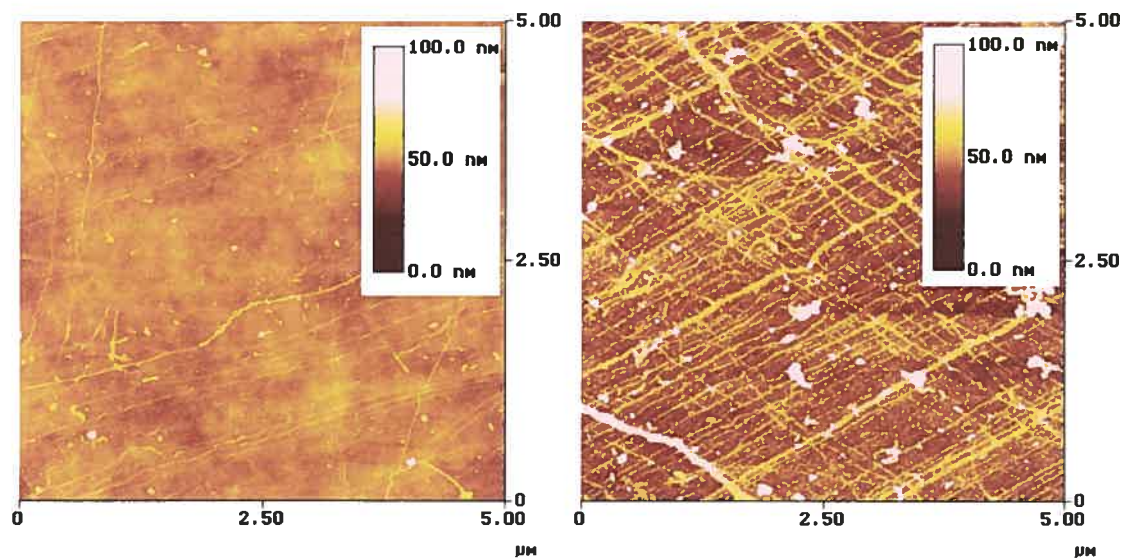
The FTIR-ATR spectrum of Nafion, Naf P1-2-0.1 and Naf P1-1-1 are shown in Figure 7.2a. The characteristic infrared bands and their assignment for the unmodified Nafion^{16,33,34} are presented in Table 7.1. The first noticeable difference between Nafion and Nafion-PANI membranes is the absence of the band associated with the H_3O^+ species at around 1710 cm^{-1} in the case of Nafion-PANI membranes. This suggests that the Nafion-PANI membranes are less hydrophilic than bare Nafion since all membranes were dried under the same conditions. Second, the presence of polyaniline at the surface of a Nafion membrane can be observed by the appearance of additional bands at around 1584 and 1493 cm^{-1} both on Naf P1-2-0.1 and Naf P1-1-1 membranes. These bands can be respectively attributed to the quinoid and benzenoid stretching modes of polyaniline.³⁵⁻³⁸ The relative intensities of these bands are indicative of the proportion of quinoid and benzenoid units. For instance,

Naf P1-1-1 seems to have around 50% of each unit whereas Naf P1-2-0.1 contains a larger proportion of benzenoid units, which suggests that PANI on Naf P1-1-1 is more oxidized than on Naf P1-2-0.1. This could be expected since Naf P1-1-1 was prepared using a higher oxidant concentration.



(a) Nafion

(b) Naf P1-1-1



(c) Nafion (5 x 5 µm)

(d) Naf P1-1-1 (5 x 5 µm)

Figure 7.1. SEM images of (a) Nafion 117 and (b) Naf P1-1-1 (bar scale represents 2 µm) and AFM images of (c) Nafion 117 and (d) Naf P1-1-1.

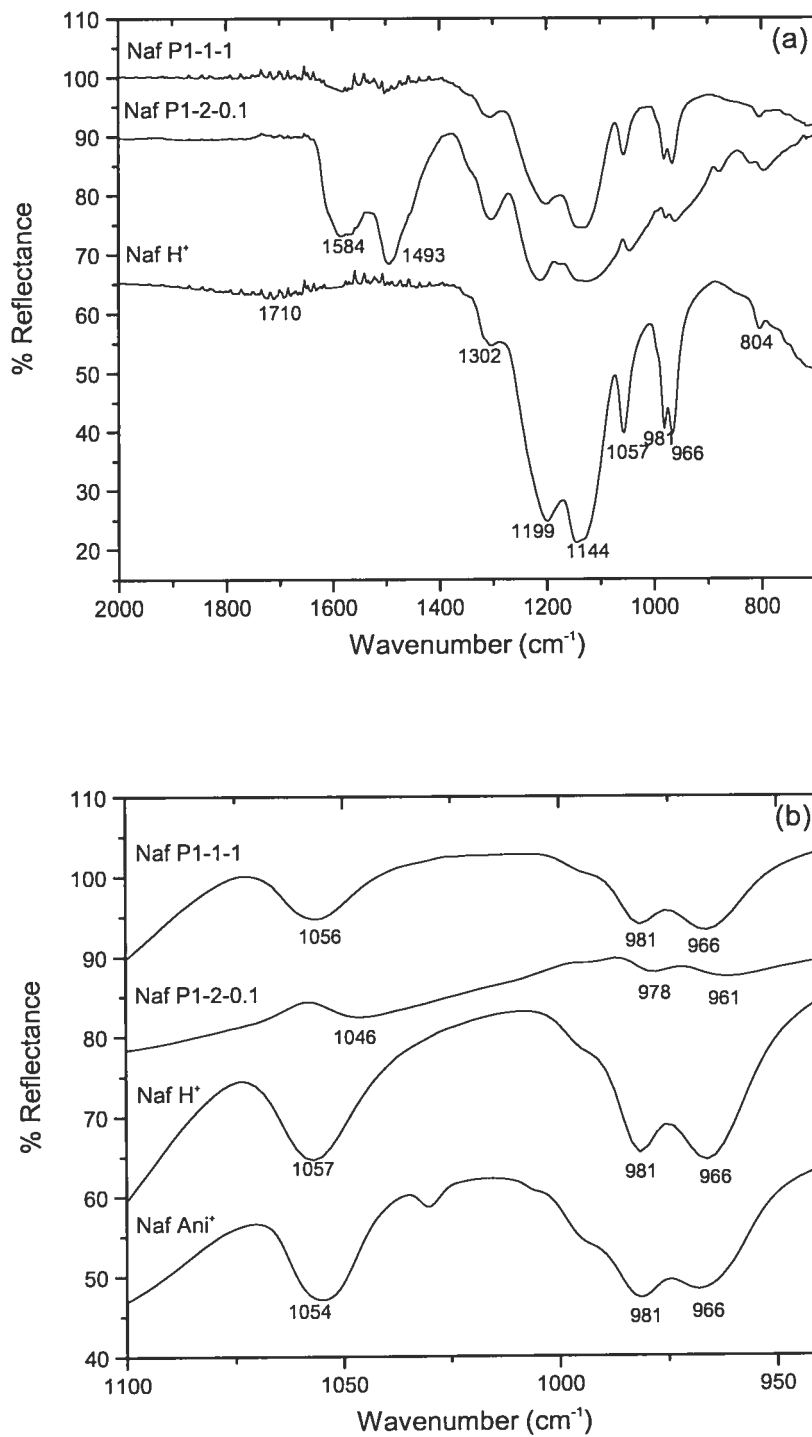


Figure 7.2. FTIR-ATR spectra of Naf P1-1-1, Naf P1-2-0.1, Nafion 117 in its protonated form (Naf H⁺) and Nafion exchanged with anilinium ions (Naf Ani⁺): (a) spectral region between 700 and 2000 cm⁻¹ and (b) between 900 and 1100 cm⁻¹.

Table 7.1. Characteristic bands observed in the FTIR spectrum of Nafion 117.

| Frequency (cm ⁻¹) | Assignment |
|-------------------------------|---|
| 1500-2050 | hydrated H ₃ O ⁺ |
| 1199 | CF ₂ asymmetric stretching |
| 1144 | CF ₂ symmetric stretching |
| 1057 | SO ₃ ⁻ symmetric stretching |
| 981 & 966 | C-O-C stretching |
| 804 | C-S stretching |

Other characteristic bands for the PANI emeraldine form (protonated by HCl) are usually found at around 1306, 1250 and 1140 cm⁻¹ assigned to C-N stretching, C-N⁺ stretching and -NH⁺= stretching, respectively.³⁵ These bands are not observable on Naf P1-1-1 due to the small amount of PANI detected at its surface, quinoid (1580 cm⁻¹) and benzenoid (1500 cm⁻¹) bands being weak. For Naf P1-2-0.1, which seems to contain a larger amount of PANI at its surface, additional features can be observed when comparing the Nafion and Naf P1-2-0.1 spectra in Figure 7.2a. The band at 1302 cm⁻¹ appears more intense and wider suggesting the presence of the C-N stretching band associated with PANI. Similarly, bands associated with the positively charged components of PANI at 1250 and 1140 cm⁻¹ are most likely superimposed on the broad CF₂ band between 1300 and 1100 cm⁻¹ since the latter band is wider than the one corresponding to Nafion.

From the infrared spectra, it is also possible to retrieve information about ionic interactions between the SO₃⁻ groups and the PANI positively charged groups. The SO₃⁻ symmetric stretching band (1057 cm⁻¹) can shift when a change in polarization of the S-O dipole is induced by its ionic environment. Lowry and Mauritz³⁹ have demonstrated that the SO₃⁻ stretching band decreases from 1073 to 1057 cm⁻¹ as the radius of the monovalent cation increases (with Li⁺, Na⁺, K⁺, Rb⁺). However, according to the same authors, this shift is observed only when Nafion contains very little water (below 7 wt %). Similarly, Lage et al.⁴⁰ have noted a shift of the SO₃⁻ band toward lower values with bivalent cations (Ca²⁺, Sr²⁺, and Ba²⁺). The shift in the SO₃⁻ stretching band has also been observed in the case of ionic interactions between SO₃⁻ groups and positively charged polymers. Tannenbaum et

al.⁴¹ have observed the SO_3^- band shift from 1059 cm^{-1} for Nafion to 1052 cm^{-1} for Nafion in the presence of a poly(ethylacrylate-co-4-vinylpyridine). They explained this shift by a lower polarization of the S-O dipole due to an increased separation between SO_3^- and H^+ following proton transfer between the sulfonate groups and positively charged pyridine units.

Figure 7.2b illustrates an enlargement of the spectral region showing the SO_3^- stretching band. It can be seen that the stretching band shifts from 1057 cm^{-1} for Nafion (Naf H^+) to 1056 cm^{-1} for Naf P1-1-1 and 1046 cm^{-1} for Naf P1-2-0.1. In the case of Naf P1-1-1, a very little shift occurs, most likely due to the small amount of PANI found at the surface of the membrane. Nevertheless, this is consistent with the band displacement observed by Park et al.¹⁶ for the interactions between polypyrrole and the Nafion SO_3^- groups. Figure 7.2b includes the corresponding infrared spectrum for Nafion exchanged with anilinium ions (Naf Ani^+). The latter shows that, as for PANI, anilinium ion interactions with SO_3^- groups decrease the frequency of its stretching band following a weaker polarization of the S-O bond. For Naf P1-2-0.1, a more important shift toward lower values is observed suggesting that a large amount of positively charged groups are interacting with the SO_3^- groups.

7.4.4. Surface chemical composition by XPS

The elemental composition determined by XPS for all membranes is given in Table 7.2. The C *1s* core level spectra of the unmodified and modified membranes are presented in Figure 7.3a. The peak envelope first shows the presence of at least two components mainly attributed to the C-C and C-H environment at low binding energy and the C-F environment at high binding energy. In fact, the C *1s* peak can be fitted with at least five components which are detailed in Table 7.3 and Figure 7.3a. The resulting peak components are consistent with those previously reported by Huang et al.⁴² After modification of the membrane, the low binding energy component increases and the C-F component decreases indicating that polyaniline is present at the surface and partially covering the Nafion membrane, as

observed by the SEM and AFM images. The C-N component of PANI can be detected at (285.5 ± 0.3) eV after curve fitting.⁴³

Table 7.2. Surface atomic composition determined by XPS.

| | %C | | %F | %O | %S | %N | %Cl | N ⁺ /N | Cl/N |
|--------------|-------------|------|------|------|-----|-----|-----|-------------------|------|
| | C-C, C-H | C-F | | | | | | | |
| Naf | 5.4 | 29.6 | 55.9 | 6.1 | 1.4 | 0 | 0 | --- | --- |
| Naf P1-2-0.1 | 39.3 | 19.3 | 29.4 | 5.7 | 0.8 | 4.8 | 1.0 | 0.30 | 0.20 |
| Naf P1-1-1 | 65.9 | 8.3 | 7.1 | 12.2 | 0.3 | 7.3 | 1.5 | 0.48 | 0.20 |

Table 7.3. Curve fitted C 1s core level spectrum components for Nafion.

| Peak Position (eV) | FWHM (eV) | Area (CPS*eV) | % of total C | Assignment |
|-----------------------|--------------|------------------|--------------|------------------------|
| 284.6 | 1.3 | 2633 | 13.2 | C-C |
| 286.3 | 1.6 | 817 | 4.1 | C-O |
| 290.4 | 1.6 | 1151 | 5.8 | ? |
| 291.5 | 1.0 | 12651 | 63.4 | CF ₂ , CF-O |
| 292.8 | 1.5 | 2579 | 13.0 | CF ₃ |

The polyaniline layer can be characterized by the N 1s high resolution spectra, illustrated in Figure 7.3b for both composite membranes. The N 1s peak can be fitted with at least three components found at 399.6, 400.8 and 402.3 eV, the first peak being attributed to -NH- and the two last peaks to positively charged nitrogen.^{26,43-45} Since the composite membranes have been conditioned in 1 M HCl prior to the XPS analysis, polyaniline is expected to be in its positively charged form. As indicated in Table 7.2, the N⁺/N ratio was found to be higher for Naf P1-1-1 than for Naf P1-2-0.1 which is consistent with the FTIR-ATR results of the quinoid/benzenoid ratio observed in Figure 7.2a. Actually, the protonation of the imines (-NH⁺=) present in the PANI chains is more favorable than for the amine groups (-NH₂⁺) since its pK_a value is 5.5 compared to 2.5 for the amine groups. Therefore, the higher the quinoid/benzenoid ratio, the higher the N⁺/N ratio will be. These data indicate once more that the PANI found on Naf P1-1-1 is more oxidized and contains more oligomers than Naf P1-2-0.1.

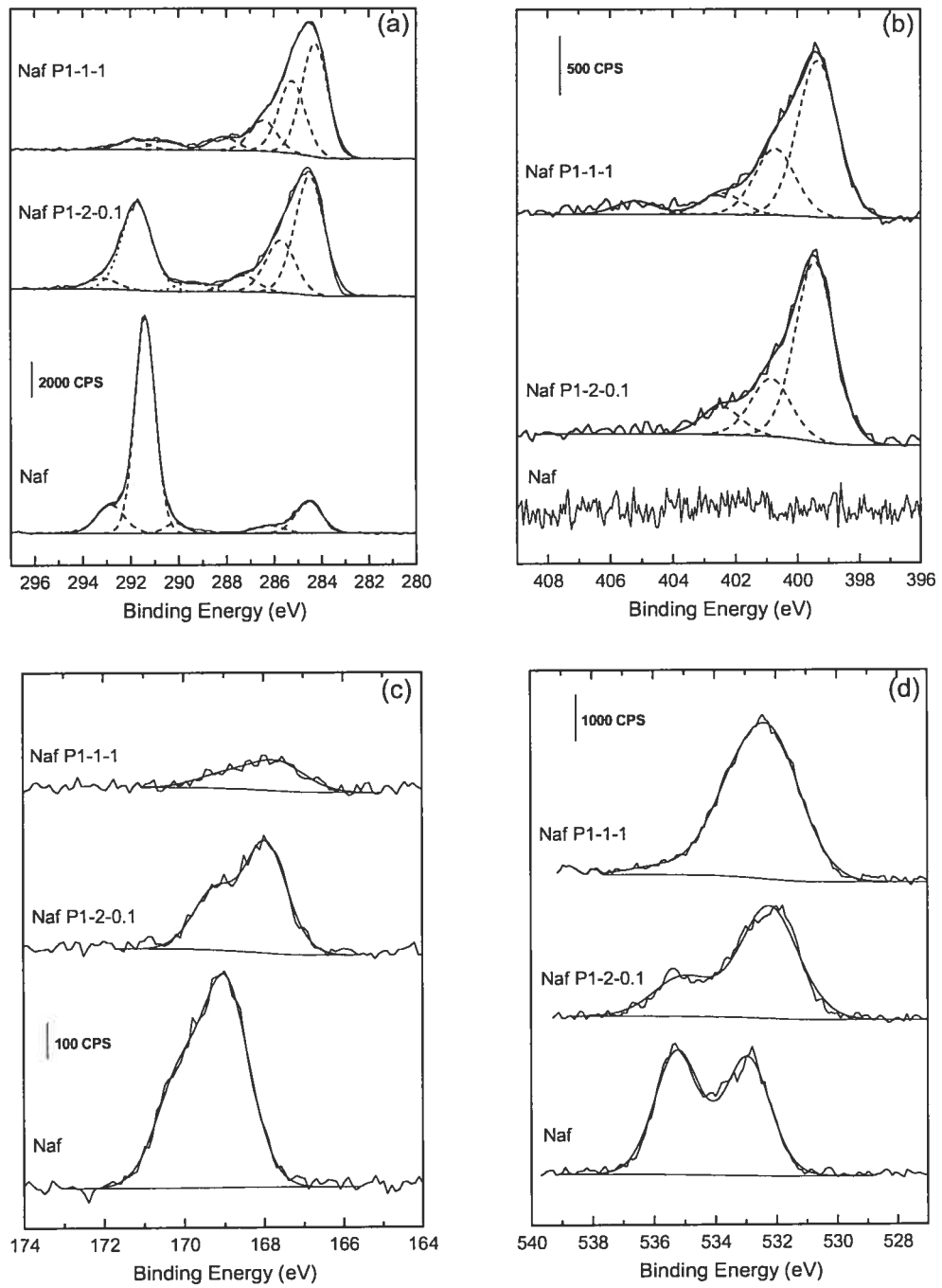


Figure 7.3. High resolution XPS spectra of the surface of Nafion and Nafion-PANI membranes: (a) C 1s, (b) N 1s, (c) S 2p and (d) O 1s.

The presence of the dopant, chloride ions, can also be detected at a binding energy of around 200 eV (not shown). The Cl/N ratio was found to be 0.20 both for Naf P1-2-0.1 and Naf P1-1-1 membranes (Table 7.2). This ratio is slightly lower than the value usually found for the emeraldine form of PANI, that is, 0.30.⁴⁶ On the other hand, since the polymerization was performed in or at the surface of Nafion, a portion of the positively charged imines or amines can be compensated by $-\text{SO}_3^-$ groups. Indeed, when comparing the S $2p$ spectrum of the unmodified membrane to the S $2p$ spectra (Figure 7.3c) of the modified membranes, a shift in binding energy is observed toward lower values in the presence of PANI. The lower binding energy values suggest the presence of interactions between the $-\text{SO}_3^-$ and $=\text{NH}^+$ - or $-\text{NH}_2^+$ -functional groups.^{24,45,47} A similar observation was noted for poly(styrene sulfonate) membranes modified with polyaniline,²⁴ and this is consistent with the FTIR results. Figure 7.3c also shows that the presence of a PANI layer at the surface of the membrane covers the Nafion sulfonate groups, lowering the S $2p$ intensity, as it was observed for the F $1s$ and C $1s$ peaks. It should be noted that in contrast to the FTIR results, XPS data suggests that more PANI is found at the surface of Naf P1-1-1 membrane than for Naf P1-2-0.1. This apparent contradiction is most likely related to the depth of analysis for both spectroscopic techniques. In fact, XPS probes only 5 to 10 nm depth whereas FTIR-ATR allows the detection of chemical species found in the first few microns.

The unmodified Nafion O $1s$ high-resolution spectrum (Figure 7.3d) exhibits two peaks centered at 533.0 and 535.3 eV attributable to sulfonic acid oxygen and ether oxygen, respectively.^{48,49} With the presence of PANI, the O $1s$ peak shape changes and the overall atomic percentage increases (Table 7.2). This was unexpected since no oxygen atom is present in PANI and the O $1s$ peak intensity was expected to be lowered as for sulfur and fluorine. Curve fitting of the O $1s$ peaks reveals the appearance of two new components in the presence of PANI. First, a peak appears at 534.1 eV which could be attributed to the sulfonate oxygen compensated by the charged imine (or amine) groups from PANI. As observed in the S $2p$ spectra of Nafion-PANI composite membranes, the presence of charged imine groups allows stabilization of the negative charge on the sulfonate group which

decreases the electron density around the oxygen atom and increases the electron density around the sulfur atom.^{24,45,47} In the case of sulfur, it was previously mentioned that the presence of PANI lowers the S 2*p* peak binding energy following the increase in electron density around the sulfur atom. In the same manner, oxygen from the sulfonate groups would possess a higher binding energy in the presence of positively charged groups. Second, Figure 7.3d illustrates the appearance of an additional peak at lower binding energy centered at 531.8 eV. We believe that this peak can be attributed to bicarbonate (HCO_3^-) adsorbed on PANI. In fact, George et al.⁵⁰ have characterized the $-\text{NH}_3^+\text{HCO}_3^-$ compound using XPS by the following peaks: 531.9 eV for the O 1*s* in HCO_3^- and 288.8 eV for the C 1*s* in HCO_3^- . When fitting the C 1*s* spectra of Nafion-PANI membranes, a peak is found at approximately 289.3 eV. This suggests that polyaniline does adsorb carbon dioxide in the presence of air and water forming HCO_3^- species. Carbon dioxide adsorption occurred although the composite membranes were dried under vacuum after their preparation (the overall sample exposition to air was less than 1 h), indicating that the $-\text{NH}_3^+\text{HCO}_3^-$ interaction is quite strong.

7.4.5. Thermogravimetric Analysis

The thermal stability of the Nafion-PANI composite membranes in comparison to the bare Nafion was studied by TGA under air atmosphere. According to the literature, thermogravimetric (TG) curves recorded under N_2 atmosphere are characterized by four phases: (i) gradual loss of water from 25 °C to ~290 °C, (ii) desulfonation (with the loss of SO_2) combined with the decomposition of the ether groups (C-O-C) on the side chains, between 290 and 400 °C, (iii) side-chain decomposition at 400 to 470 °C and (iv) decomposition of the poly(tetrafluoroethylene) backbone at 470 to 560 °C.^{51,52} Figure 7.4 illustrates the TG and differential thermogravimetric (DTG) curves of Nafion, Naf P1-1-1 and Naf P1-2-0.1 recorded under air atmosphere. The Nafion DTG curve (Figure 7.4b) exhibits transitions at the temperature ranges of 25-250 °C, 290-390 °C, 390-475 °C and 475-545 °C which are in concordance with the four decomposition stages given

in the literature and described above. Only the PTFE backbone decomposition occurs at a lower temperature range due to the presence of air. After polymerization of aniline on Nafion membranes, it can first be observed that the modified membranes contain less water (18%) than the bare Nafion (23%) and this is consistent with the FTIR-ATR spectra (Figure 7.2a) showing that the presence of PANI decreases the hydrophilicity of the membrane. Second, the Nafion-PANI membrane DTG curve indicates that the degradation of the sulfonate groups starts at a lower temperature than for the bare Nafion and seems to occur in two stages, according to Figure 7.4b. The first stage starts at 265 °C for both membranes and the second stage starts at around 335 °C for Naf P1-1-1 and 325 °C for Naf P1-2-0.1. The two different stages could be attributed on one hand to SO_3^- and C-O-C decomposition occurring in the presence or absence of PANI. On the other hand, the two stages could also be associated with the SO_3^- interacting with PANI and the C-O-C decomposition occurring separately. Actually, the weight percent (wt %) lost up to the temperature between both peaks corresponds approximately to the wt % associated with sulfur when calculated with the IEC values and this supports the latter hypothesis. Nonetheless, care should be taken in the interpretation of the decomposition stages since they do not necessarily occur separately, and different functional groups can degrade simultaneously. As for the side-chains and backbone decomposition of the Nafion-PANI membranes, it occurs in the same temperature range for Naf P1-2-0.1, as opposed to Naf P1-1-1, for which it is shifted to higher temperatures. The difference between both Nafion-PANI composite membranes could be related to the chain length of PANI and/or to the location of the PANI chains within the Nafion matrix. Indeed, Nafion exchanged with anilinium ions ($\text{C}_6\text{H}_5\text{-NH}_3^+$), identified as Naf-Ani⁺, also exhibits this shift toward higher temperature for the side-chains and backbone degradation (Figure 7.4b). Rollet et al.⁵³ have previously demonstrated that ammonium ions tend to diffuse in the intermediate phase of Nafion composed of ether side chains. Thus, if most of the PANI chains found in the Naf P1-1-1 are located in the intermediate phase with the positively charged groups oriented toward the sulfonic acid clusters, as it would be for anilinium ions, then it could change the morphology and thermal stability of these

side chains. This would explain the shift toward higher temperatures observed in the degradation of the side-chains for both Naf-Ani⁺ and Naf P1-1-1. Hence, Naf P1-1-1 could contain a large amount of oligomers which would have similar interactions with the Nafion membrane as the anilinium ions and thus, leading to a similar Nafion morphology. In fact, the presence oligomers in Naf P1-1-1 was previously evidenced by the observation of a pink coloration around the modified area of the membrane, the higher quinoid/benzenoid and N⁺/N ratios.

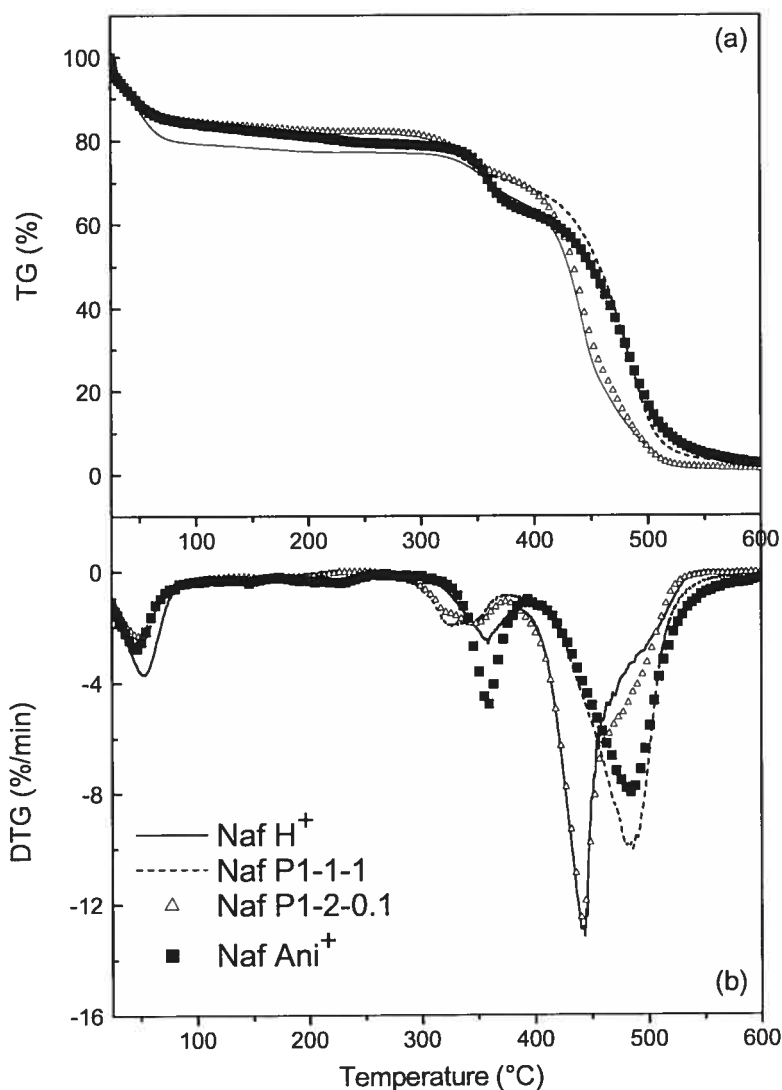


Figure 7.4. Thermogravimetric analysis curves of Nafion 117 in its protonated form (Naf H⁺), Naf P1-1-1, Naf P1-2-0.1 and Nafion exchanged with anilinium ions.

7.4.6. Differential Scanning Calorimetry

DSC thermograms of Nafion can reveal information about the states of water found in the membrane as well as the SO_3^- cluster transitions. First, it is known that three different states of water are generally found in ionomers such as Nafion membranes: (i) unbound freezable water, (ii) bound freezable water, and (iii) unfreezable water.^{54,55} The unbound freezable water behaves much like bulk water and is not interacting with the polymer; the bound freezable water is the water found inside the pores or clusters of the polymer but not strongly associated with the polymer contrarily to unfreezable water, which would be strongly associated with the polymer and for which it is not possible to observe the crystallization and melting transitions. Figure 7.5a shows the first cooling curves obtained with the Nafion and Nafion-PANI composite membranes. Nafion presents an exothermic peak at around $-20\text{ }^\circ\text{C}$ associated with the crystallization of water. This crystallization temperature is in agreement with values published by other researchers.^{56,57} Since the crystallization temperature is below 0°C , it can be qualified as bound freezable water. This supercooling effect has been reported in the literature with different hydrophilic polymers, such as cellulose and hydroxymethacrylates derivatives,^{54,58} and is caused by the interactions of the water molecules with the hydrophilic units or ionic sites.

Water in Naf P1-1-1 composite membranes seems to behave in the same manner as for the unmodified Nafion since water freezes at approximately the same temperature but over a wider range. The effect of PANI is more important in the case of Naf P1-2-0.1 where the peak is clearly split in two. This splitting was previously observed by Saito et al.⁵⁷ and Asaka et al.⁵⁵ for different perfluorosulfonic acid membranes exchanged with various counter ions. They have explained this splitting by the presence of different states of water. In addition, Asaka et al. have suggested that the freezable bound water is actually found in the ionic clusters of Nafion. Thus, if the latter hypothesis is true, it could imply that Naf P1-2-0.1 contains PANI chains or aggregates inside the ionic clusters which would affect the state of water present, resulting in a split crystallization peak.

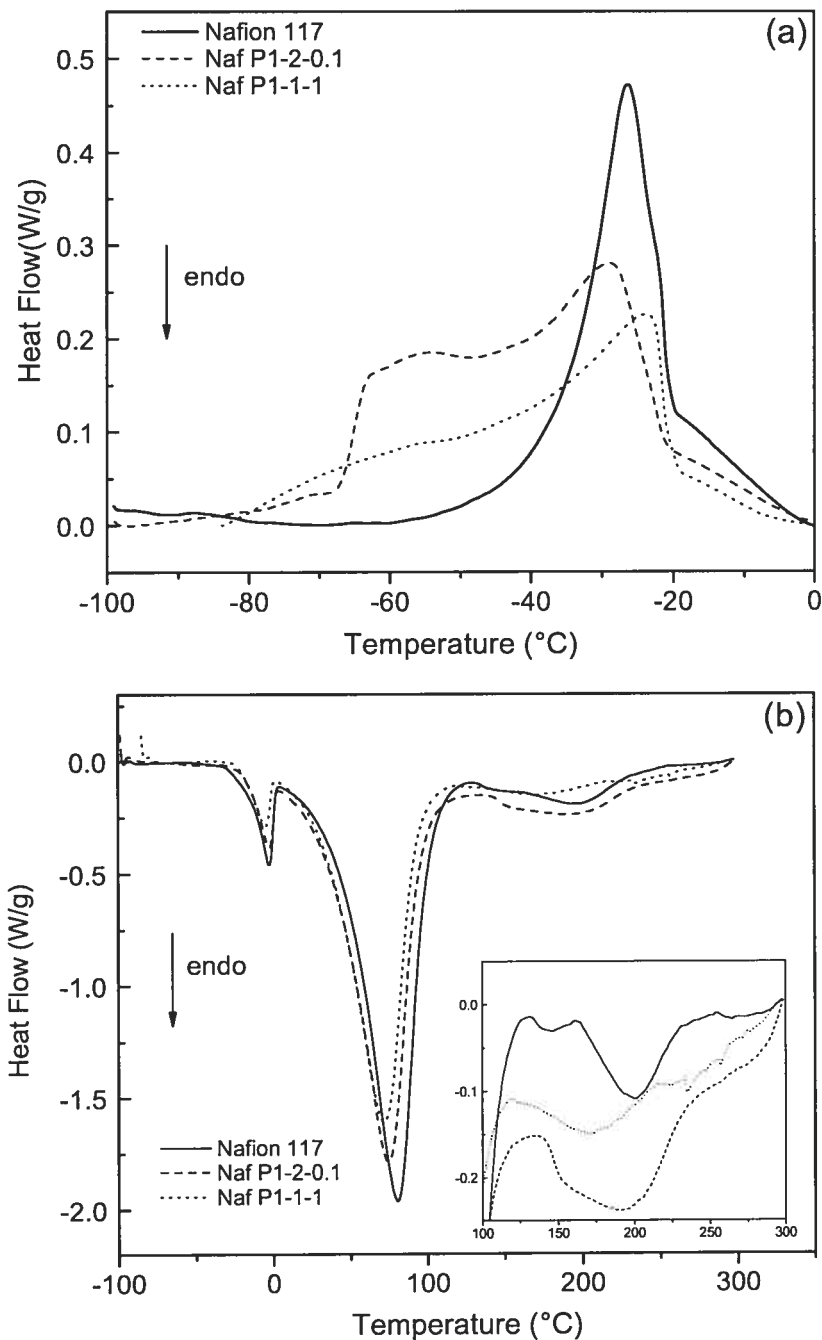


Figure 7.5. DSC first cooling (a) and heating (b) curves of Nafion 117, Naf P1-2-0.1 and Naf P1-1-1 membranes. The inset is an expansion of the region between 100 and 300°C. Measurements were recorded under helium atmosphere.

Regarding the heating curves, the peak maxima for the melting and vaporization of freezable water are observed at around -5°C and 70°C , respectively (Figure 7.5b). The vaporization temperature is the same as the one obtained by TGA (Figure 7.4b). In addition, the region above 100°C shows two endothermic peaks interpreted as a cluster transition at 146°C and melting of the non polar crystallite backbone at 200°C .⁵⁹ Once modified, the cluster transition temperature of Nafion increases whereas the melting temperature decreases. These tendencies are consistent with those observed by Park et al. for Nafion membranes modified with polypyrrole.¹⁶ It is plausible to assume that the presence of PANI forces the Nafion polymer chains to re-organize themselves and form a more cross-linked structure within the clusters which would increase the cluster transition temperature.

7.4.7. Membrane Transport Properties

As mentioned in the Introduction, the main objective in modifying the Nafion membranes with polyaniline is to block the transport of Zn^{2+} during electro dialysis in acidic media. Therefore, to evaluate the blocking behavior of the Nafion-PANI composite membranes toward bivalent cations, electro dialysis assays using a two-compartment cell were performed. Table 7.4 gives the Zn^{2+} leakage percentage obtained for the unmodified and modified membranes. The membrane modification with polyaniline seems to improve its blocking behavior for the transport of Zn^{2+} , since after modification, the Zn^{2+} leakage drops from 11 to 5% for Naf P1-1-1 and to $< 0.5\%$ for Naf P1-2-0.1. However, the decrease in Zn^{2+} leakage is associated with a loss in ionic conductivity, and in fact, the ionic conductivity decreases proportionally with the Zn^{2+} leakage. This loss in conductivity has been previously reported by several teams working on the modification of Nafion for reducing the methanol crossover in direct methanol fuel cells.^{13,16,17} The linear relationship between zinc leakage and ionic conductivity could suggest that PANI chains are partially blocking the ionic cluster network by reducing the number of ion-exchange sites. Indeed, some interactions exist between the positively charged PANI chains and the sulfonate groups, as demonstrated by the FTIR-ATR, XPS, DSC, and TGA results

described above. On the other hand, Table 7.4 shows that the IEC value for Naf P1-1-1 is lower than for Naf P1-2-0.1 while the conductivity of the latter is significantly lower. The weight increase associated with the amount of PANI, which is only slightly higher for Naf P1-1-1 than for Naf P1-2-0.1 (Table 7.4), cannot explain why the Naf P1-1-1 IEC value is much lower. An explanation for this contradictory result is proposed below. Table 7.4 also shows that the amount of water decreases with the small increase in the amount of PANI, which is consistent with the FTIR-ATR and TGA results.

Table 7.4. Membrane physical properties and transport behavior.

| | Zn ²⁺ leakage (%) ±0.5 | σ (mS/cm) | IEC (mmol/g) | H ₂ O (wt.%) ±1 | PANI (wt. %) ±1 |
|--------------|---|---------------------|-----------------|----------------------------------|-----------------------|
| Nafion | 11 | 136 | 0.93 ± 0.04 | 26 | --- |
| Naf P1-2-0.1 | < 0.5 | 6.5 | 0.90 ± 0.08 | 25 | 2.7 |
| Naf P1-1-1 | 5 | 65.2 | 0.78 ± 0.04 | 24 | 3.3 |

7.5. DISCUSSION

7.5.1. Microstructure of Nafion-PANI composite membranes

To better understand the relationship between the presence of PANI in Nafion and the transport properties of the composite membranes, it would be useful to try to determine the location of PANI within the structure of Nafion. Nafion is structurally composed of three regions: (i) the poly(tetrafluoroethylene) backbone which is very hydrophobic; (ii) the hydrophilic ionic sites (SO₃⁻) and (iii) an intermediate region containing the ether side chains. Several studies have been reported on the morphology of Nafion since the early 1980s. Mauritz and Moore have recently published a complete review on the models describing the morphology of Nafion.³⁰ Among others, there is the well-known cluster-network model, developed by Gierke et al.^{60,61} in 1982, suggesting the presence of hydrophilic ionic clusters linked together by ionic channels, which allow the transport of ions, in a hydrophobic

matrix. Since then, other models have been suggested such as the core-shell structure with an ion-rich core (Fujimura et al.⁶²), the hard sphere model (Kumar and Pineri,⁶³ Orfino and Holdcroft⁶⁴) and the lamellar model (Litt⁶⁵). In the more recent years, studies tend to suggest that the ionic sites are grouped together in rodlike or ribbonlike structures and that these ionic aggregates might be linked together by only one SO_3^- group instead of channels.³⁰ Up to now, the morphology of Nafion is still not completely elucidated, and there is not a general agreement on the Nafion structure. Nevertheless, it is generally agreed that the ionic sites can reorganize themselves depending on the hydration level of the polymer. It is also known that there is a hydrophilic path through which water and ions are transported.

The modification of Nafion membranes by in-situ polymerization of aniline will certainly affect the microstructure of the membrane. For instance, it is believed that a portion of the PANI chains are present in the hydrophilic clusters since the ionic transport is partially inhibited. However, the two Nafion-PANI composite membranes seem to present different microstructures as well as physical and transport properties. First, XPS data suggest that Naf P1-1-1 has more PANI at its surface than Naf P1-2-0.1. On the other hand, FTIR-ATR data demonstrates the opposite but, as explained earlier, this is probably due to the difference in depth of analysis between XPS and FTIR-ATR. In addition, the different results obtained with these two surface techniques suggests that the PANI layer in Naf P1-1-1 is most likely found at the surface of the membrane. Second, FTIR-ATR, DSC, electro dialysis, and conductivity results suggest that Naf P1-2-0.1 contains more PANI inside the ionic clusters. The difference between both Nafion-PANI composite membranes is most likely related to the polymerization conditions. In the case of Naf P1-1-1, the high oxidant concentration (1 M) and short reaction time (1 h) would favor the relatively fast polymerization of aniline at the surface of the Nafion membrane. Zawodzinski et al.⁶⁶ have demonstrated by contact angle measurements that when Nafion is in contact with liquid water, a high concentration of SO_3^- groups are at the interface of Nafion and water; however, when in contact with saturated vapor water, the surface is rich in fluorinated carbon chains. Hence, when protons are exchanged with anilinium ions, during the first step of the modification,

anilinium ions can be found at the surface. Upon addition of the oxidant, polymerization will first occur at the surface. Moreover, the negative charge of the oxidant, $S_2O_8^{2-}$, will most likely keep the oxidant from diffusing through the Nafion cation-exchange membrane resulting in the formation of PANI at the surface of Nafion. In contrast, Naf P1-2-0.1 is prepared using a low oxidant concentration (0.1 M) and a longer reaction time (2 h). The low concentration of oxidant would slow the polymerization process, allowing the oxidant to penetrate the membrane through the hydrophilic channels or path as the positively charged PANI chains are formed in the hydrophilic ionic clusters. It is also possible to imagine that the $-SO_3^- \dots ^+H_3N-C_6H_5$ ionic pair is reorientated toward the bulk of the membrane as the polymerization proceeds to favor the interactions of the PANI chains with the intermediate phase, which would be thermodynamically favorable. Indeed, the PANI chains could be located either in the intermediate region between the hydrophobic and the hydrophilic region, as it was demonstrated by small-angle neutron scattering measurements for $N(CH_3)_4^+$ ions,⁵³ or in the hydrophilic clusters.

The observed differences in morphology between both Nafion-PANI composite membranes could explain why the IEC of Naf P1-1-1 is lower than the IEC of Naf P1-2-0.1 despite the fact that it does not block as efficiently the transport of cations. In fact, to completely block the transport of cations through the membrane, it is only necessary to disrupt all the channels through which the ions are transported. Thus, if the PANI chains are mostly formed in the channels, such as in the case of Naf P1-2-0.1, it is possible that they simply block more ion transport channels than Naf P1-1-1. The latter probably contains about the same amount or maybe a little more PANI chains or oligomers than Naf P1-2-0.1 (Table 7.4), but PANI is present mostly at the surface of the membrane without blocking entirely the ion channels. Furthermore, Naf P1-1-1 contains more short chains or oligomers of PANI as evidenced by the higher quinoid/benzoid and N^+/N ratios obtained by FTIR-ATR and XPS, respectively. These short chains could also diffuse inside the membranes and reduce the IEC of the membrane without totally blocking the transport of cations. The latter hypothesis was also suggested to explain the

relatively high decomposition temperature of the Nafion side-chains observed by TGA.

7.5.2. Comparison with Poly(styrene sulfonate)-PANI Composite Membranes

In our previous work, we have characterized the poly(styrene sulfonate)-polyaniline composite membranes prepared in a similar fashion.²⁴⁻²⁶ Thus, it could be interesting to compare the physical and ion transport properties of these composite membranes with those of the Nafion-polyaniline membranes. The first observation made during the modification of the membranes is that it is much more difficult to obtain a uniform and thin PANI layer on the Nafion membrane. For example, a Nafion-PANI membrane prepared using 1-h oxidation time and a 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution as the oxidizing agent (Naf P1-1-0.1), which had a transparent green color, did not present any significant blocking behavior toward Zn^{2+} ions (10% Zn^{2+} leakage). In addition, although a dark PANI layer is obtained, as in the case of Naf P1-1-1 and Naf P1-2-0.1, SEM (Figure 7.1) and XPS (Figure 7.3) results show that a total coverage of the surface of Nafion cannot be obtained. In contrast, visually transparent and uniform layers of PANI can be formed at the surface of Neosepta CMX membranes as previously reported.²⁶ At a smaller scale, the AFM images represented in Figure 7.6b also show that the PANI morphology is porous as opposed to the fibril-like structure obtained on Nafion and shown in Figure 7.1d. The difference in the nature of the substrate has an impact on the nature of the layer at the surface of the composite membranes. The perfluorocarbon chains of Nafion are very hydrophobic as compared to anilinium species and do not contain any phenyl rings that provides some π -stacking interactions such as in the case of poly(styrene sulfonate) substrates.^{24,26}

Another point of interest is to compare how the presence of PANI affects the membrane permselectivity for protons against Zn^{2+} . In the present work, the results suggest that the composite membrane having the best blocking behavior is the membrane containing PANI into the ionic clusters which interrupts the ionic path through the membrane. In contrast, it was previously demonstrated for the

CMX-PANI composite membrane that only a very thin but uniform layer of PANI at the surface of the membrane is required to block efficiently the transport of Zn^{2+} without significantly decreasing the proton conductivity.²⁴⁻²⁶ The differences observed between both types of composite membranes with respect to the transport property behavior can be explained by the morphology of the polymer membrane itself. As described above, Nafion is known to phase separate into hydrophobic and hydrophilic regions with an intermediate phase containing the ether side-chains. Thus, ions are most likely being transported through the ionic channels or ionic clusters. The phase separation of the ionic species explains why Nafion has a high ionic conductivity when compared to that of other ionomers. Poly(styrene sulfonate) possesses a more rigid structure and does not allow the sulfonic acid groups to reorganize themselves into a separate phase. For this reason, sulfonic acid groups are probably more randomly dispersed through the polymer of the CMX membrane.

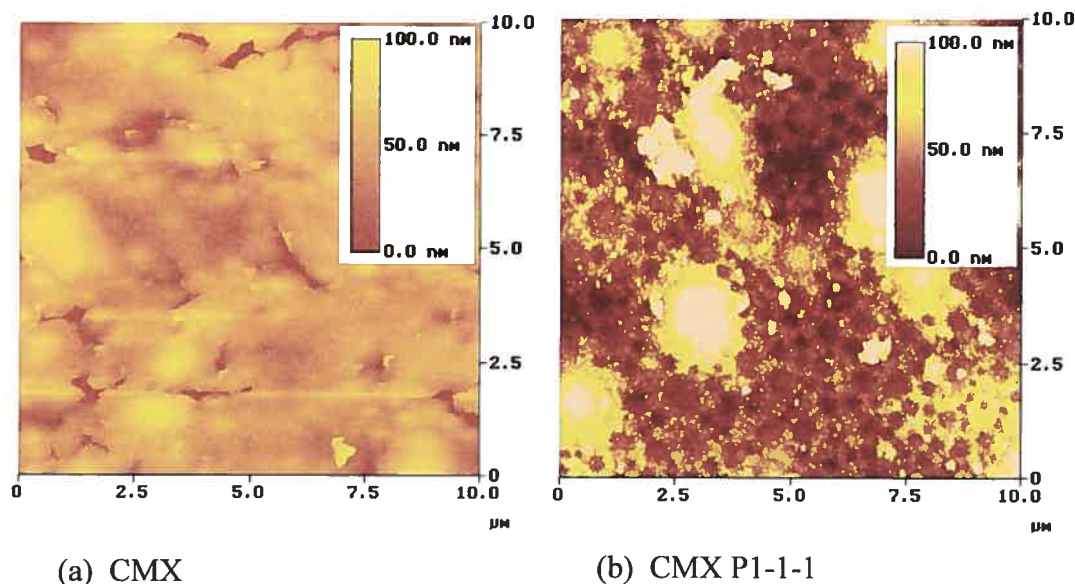


Figure 7.6. AFM images of (a) unmodified CMX and (b) PANI modified CMX membranes.

7.6. CONCLUSION

To summarize, the main goal of this work was to characterize the Nafion-PANI composite membranes to afford a better understanding of the Nafion microstructure after modification with polyaniline. From the data obtained, we believe that, depending on the polymerization conditions, it is possible to prepare a Nafion-PANI composite membrane with shorter PANI chains mainly found in the intermediate phase of Nafion (with high oxidant concentration and short polymerization time) and a composite membrane with longer PANI chains mostly found inside the ionic clusters or channels (with low oxidant concentration and longer polymerization time). In addition, it is demonstrated that the ionic transport of both H^+ and Zn^{2+} will be dependent on the amount of polyaniline disrupting the ionic paths and not necessarily the total amount of PANI. The amount of PANI found in the ionic paths area would in turn depend on the chain length of PANI and the polymerization conditions. Hence, this study gives an insight on how the presence of polyaniline could affect the Nafion morphology and transport properties. It could contribute to understanding the factors involved in the ionic transport through Nafion membranes and in the development of cation-exchange membranes for fuel cells.

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7.8. INFORMATION AVAILABLE IN ANNEXE II

Pictures of modified membranes obtained under different polymerization conditions are provided in Annexe II.

7.9. REFERENCES

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Chapitre 8

Conclusion générale
et
perspectives de travail

8.1. CONCLUSION GÉNÉRALE

L'objectif principal de ce travail était d'améliorer la permselectivité et d'étudier les facteurs impliqués dans le comportement permselectif des membranes échangeuses de cations pour les cations monovalents face aux cations bivalents lors des électrodialyses en milieu acide. Pour ce faire, des membranes échangeuses de cations commerciales ont été modifiées par polymérisation in situ de l'aniline en milieu aqueux. La modification des membranes est effectuée dans une cellule à deux compartiments soit en deux étapes (chapitres 3 à 7) qui consiste à ajouter les réactifs d'un seul côté de la membrane, soit en une étape (chapitre 5) en ajoutant l'aniline et l'oxydant de part et d'autre de la membrane à modifier. Les méthodes de modification employées dans ce projet permettent de polymériser l'aniline sur une seule face de la membrane. Le fait de former la PANI sur une seule face permet de diminuer la quantité de PANI formée dans la matrice de la membrane commerciale, évitant ainsi de transformer la membrane échangeuse de cations en membrane échangeuse d'anions et de maintenir une conductivité ionique pour les protons suffisamment grande.

Tout d'abord, avant de tenter de comprendre le comportement des membranes composites contenant de la polyaniline, des études préliminaires ont été effectuées dans le but de démontrer que la polyaniline affectait le comportement sélectif des membranes commerciales durant les électrodialyses de métaux bivalents en milieu acide. Le chapitre 3 démontre qu'effectivement, la présence de polyaniline polymérisée au sein d'une membrane Neosepta CMX, une membrane à base de poly(styrène sulfonate), permet de bloquer le transport du Zn^{2+} et Cu^{2+} . Le chapitre 3 introduit également les techniques permettant de détecter la polyaniline à la surface de la membrane. Entre autres, il est possible de voir par microscopie électronique à balayage que les membranes CMX ayant de la PANI à leur surface présentent une surface davantage rugueuse que la CMX. La spectroscopie des photoélectrons-X permet quant à elle de démontrer de façon semi-quantitative la présence de la PANI à la surface des membranes par l'augmentation du signal N $1s$ et la diminution du

signal S 2p. Cette dernière observation est expliquée par le fait que les groupements sulfonates présents à la surface de la CMX sont recouverts par une couche de PANI.

Afin de mieux maîtriser la polymérisation de l'aniline sur la membrane CMX, le comportement sélectif des membranes CMX-PANI a été étudiée en fonction de deux paramètres de polymérisation, soit le temps d'échange des ions anilinium (Chapitre 3) et le temps d'oxydation ou de polymérisation (Chapitre 4). Dans le premier cas, aucun changement dans le comportement permselectif de la membrane n'est observé après une heure d'échange en présence d'une solution de 1 M aniline préparée dans 1 M HCl. Dans le deuxième cas, le taux de fuite en cations bivalents semble dépendre grandement du temps d'oxydation choisi et des conditions de polymérisation en général. En effet, une caractérisation par SEM, XPS, voltammétrie cyclique et spectroscopie UV/Visible démontre que l'utilisation d'un temps court d'oxydation mène à la formation d'une couche de PANI à la surface de la membrane CMX, qui permet de bloquer le transport des cations bivalents. Tandis qu'à des conditions extrêmes d'oxydation de l'aniline, c'est-à-dire avec une solution de 1 M de persulfate d'ammonium et un temps supérieur à 1 h, il y a dégradation graduelle du film de PANI formé à la surface de la membrane CMX et formation de courtes chaînes de PANI à l'intérieur de la membrane. Or, la présence de ces courtes chaînes de PANI à l'intérieur de la membrane ne semble pas être suffisante pour bloquer le transport des cations Zn^{2+} et Cu^{2+} lors des électrodialyses. Par ailleurs, un modèle d'interface entre la polyaniline et la membrane CMX est proposé dans le chapitre 4.

Toujours dans le but de mieux comprendre les facteurs impliqués dans le mécanisme de blocage du transport des ions bivalents à travers les membranes composites poly(styrène sulfonate)/poly(aniline), d'autres conditions de polymérisation ont été étudiées dans le chapitre 5. La concentration et la nature de l'oxydant, de même que la méthode de modification, ont été modifiées dans ce chapitre. Dans un premier temps, une concentration plus faible en oxydant est utilisée dans le but d'obtenir une couche plus mince de PANI et ainsi, réduire la résistance au transport des protons. En utilisant une concentration de 0.3 M de persulfate d'ammonium, une couche transparente et homogène de PANI est formée à

la surface de la membrane CMX. Cette membrane composite contenant très peu de PANI (moins de 1 % en masse) permet de bloquer le transport des ions Zn^{2+} aussi efficacement que les membranes contenant davantage de PANI à la surface, présentés dans les chapitres précédents. Ainsi, ceci démontre qu'il suffit d'une couche de PANI homogène, mais pas nécessairement épaisse, pour bloquer le transport des ions Zn^{2+} .

Dans un deuxième temps, les résultats du chapitre 5 montrent qu'il est possible de contrôler le lieu de polymérisation de l'aniline au sein de la membrane en utilisant différents oxydants et une nouvelle méthode de modification. En employant la méthode de modification en une étape avec des oxydants possédant une charge négative ($S_2O_8^{2-}$) ou une charge positive (Fe^{3+}), il est possible d'obtenir une couche de PANI à la surface ou à l'intérieur de la membrane CMX. Or, il est démontré que la présence de PANI à la surface de la membrane est essentielle pour bloquer le transport des ions Zn^{2+} lors des électrodialyses. En effet, les membranes CMX-PANI préparées avec le Fe^{3+} et possédant une couche de PANI à l'intérieur de la membrane ne semblent pas bloquer le transport des ions Zn^{2+} . Par ailleurs, les résultats du chapitre 5 laissent croire que le processus de blocage des ions Zn^{2+} lors des électrodialyses est un phénomène électrostatique plutôt que physique. Autrement dit, la charge positive des groupements imines et amines sur les chaînes de PANI jouerait un rôle plus important dans le blocage du transport des ions Zn^{2+} que la réduction de la porosité de la membrane suite à l'ajout d'un polymère à la surface de celle-ci.

Le chapitre 6 présente une étude de stabilité de la membrane CMX-PANI. L'analyse thermogravimétrique démontre que la présence de la polyaniline ne semble pas affecter la stabilité thermique de la membrane. La membrane CMX-PANI, semble également être stable chimiquement, puisque après une série de quinze électrodialyses, la membrane composite semble maintenir ses propriétés perméables, avec un taux de fuite en Zn^{2+} inférieur à 0.1%. Cependant, la membrane semble moins performante lorsqu'une électrodialyse de longue durée est effectuée. Après 48 h d'électrodialyse, la membrane donne un taux de fuite en Zn^{2+} d'environ 2.3%. Cette perte de perméabilité est probablement causée par une charge excessive de Zn^{2+} à l'interface de la membrane, ce qui confirmerait que le

processus de blocage du transport des ions Zn^{2+} est un phénomène plutôt électrostatique que physique.

La dernière partie de ce projet avait pour but d'appliquer les connaissances acquises dans les chapitres précédents dans la préparation de membranes composites Nafion-PANI et de comparer son comportement permselectif aux membranes CMX-PANI. Ainsi, les membranes Nafion-PANI ont été caractérisées par SEM, AFM, FTIR-ATR, XPS, DSC, TGA, électrodialyse, mesures de conductivité et de capacité d'échange ionique. Les résultats suggèrent la possibilité de former de la poly(aniline) à l'intérieur des agrégats ioniques du Nafion dans des conditions douces de polymérisation, c'est-à-dire en employant une concentration faible en oxydant (0.1 M persulfate d'ammonium) et des temps de polymérisation suffisamment longs afin de former une couche de PANI homogène. La formation de PANI à l'intérieur des agrégats ioniques bloque la voie de transport ionique des cations et donc, diminue le transport des ions Zn^{2+} durant les électrodialyses (le taux de fuite étant inférieur à 0.5%). Par opposition, les résultats de FTIR-ATR, XPS, DSC et TGA semblent suggérer que l'utilisation d'une solution plus concentrée d'oxydant (1 M persulfate d'ammonium) favorise plutôt la formation de courtes chaînes de polyaniline présentes davantage à la surface de la membrane et dans la phase intermédiaire du Nafion. Rappelons ici que la phase intermédiaire est la zone entre la phase ionique, formée des groupements sulfonates, et la phase hydrophobe, composée des chaînes de poly(tétrafluoroéthylène). Cependant, une proportion de ces chaînes de PANI dans cette dernière membrane se retrouve probablement dans les régions ioniques, car le taux de fuite en Zn^{2+} est tout de même réduit de moitié par rapport à la membrane Nafion non-modifiée.

La comparaison des résultats obtenus avec les membranes composites Nafion-PANI avec ceux de la CMX-PANI semble démontrer que la PANI bloque de façon différente le transport des ions Zn^{2+} lors des électrodialyses en milieu acide. Comme il est suggéré dans les chapitres 5 et 6, la présence des charges positives sur la chaîne de poly(aniline) semble jouer un rôle important dans le blocage du transport du Zn^{2+} avec les membranes CMX-PANI, la poly(aniline) agissant davantage comme une barrière électrostatique de physique. Au contraire, dans le cas des membranes

Nafion-PANI, c'est plutôt un blocage physique de la voie de transport des cations, formée par les agrégats ioniques, qui permet d'empêcher le transport des cations bivalents. Le fait de bloquer les voies de transport ionique rend cependant la membrane inutilisable pour l'application visée, car la conductivité des protons sera diminuée de manière proportionnelle à la conductivité des ions Zn^{2+} à travers la membrane, ce qui n'est pas le cas des membranes CMX-PANI. Cette différence est principalement attribuable à la différence en morphologie entre les membranes à base de poly(styrène sulfonate) et de Nafion.

En conclusion, selon les résultats obtenus dans ce projet, les membranes composites possédant les meilleures propriétés de sélectivité pour le transport des ions H^+ face aux cations bivalents, particulièrement le Zn^{2+} et le Cu^{2+} , semblent être celles à base de poly(styrène sulfonate)/poly(aniline). Ces membranes permettent d'obtenir des taux de fuite en Zn^{2+} et Cu^{2+} pouvant être inférieurs à 0.1%, une valeur comparable et même inférieure à celle des membranes commerciales permselectives aux cations monovalents. De plus, les membranes composites CMX-PANI semblent posséder une bonne stabilité pour les électrodialyses de courte durée en milieu acide. Évidemment, dans le but d'évaluer l'applicabilité de ces membranes aux différents procédés d'électrodialyse et d'améliorer la stabilité de ces membranes, plusieurs travaux peuvent être envisagés.

8.2. PERSPECTIVES DE TRAVAIL

Une étude de conductivité de différents cations métalliques ou organiques possédant différentes charges ioniques et différentes taille pourrait permettre d'évaluer la résistance ionique en fonction de ces différents paramètres. En fait, les mesures d'électrodialyses ne permettent pas toujours de bien différencier les propriétés de transport ionique de la membrane. Par exemple, dans le chapitre 4, quelques électrodialyses ont été effectuées avec le Cu^{2+} en comparaison avec le Zn^{2+} , mais peu de différences ont été observées en terme de sélectivité. Les mesures de conductivité, pouvant être effectuées à de faibles concentrations ioniques, pourraient

permettre d'évaluer la sélectivité relative des membranes composites pour ces deux cations bivalents. De même, des mesures de conductivité et des électrodialyses pourraient être effectuées avec des solutions acides contenant un mélange de métaux. Et puisque les électrodialyses ont été effectuées dans une cellule à deux compartiments, il serait intéressant d'évaluer la performance de notre membrane composite dans une cellule d'électrodialyse à plusieurs compartiments avec un système d'écoulement continue, telle que les cellules utilisées en industrie (schématisées à la Figure 1.7).

Pour améliorer les performances des composites Nafion-PANI au niveau de la conductivité des protons, il serait envisageable de modifier les membranes Nafion par co-polymérisation in situ de l'aniline avec une aniline sulfonate (acide o-, m- ou p-aminobenzènesulfonique) en petite quantité. En introduisant des groupements sulfonates dans la chaîne de polyaniline, une meilleure conductivité ionique des protons devrait être observée par rapport à la présence de polyaniline non sulfonée.

D'autre part, il serait pertinent de réaliser des études de diffusion des différents oxydants et de l'aniline à travers la membrane Nafion pour éventuellement contrôler le lieu de polymérisation de l'aniline au sein de cette membrane, comme ce qui a été réalisé dans le cas des membranes CMX-PANI (chapitre 5).

Annexe I

Matériel supplémentaire au chapitre 4

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Characterization of a Cation-Exchange/Polyaniline Composite Membrane

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To compensate for charging effects, binding energy values had to be calibrated. The C $1s$ peak is usually calibrated at 284.5 eV. However, this was not possible since the carbon nature changed drastically depending on whether it was in presence or in absence of PANI. For the unmodified membrane, the major carbon contribution was influenced by the presence of covalent chlorine from poly(vinyl chloride), the supporting material of the membrane. In the case of CMX P1-1, the major carbon contribution originated from polyaniline. The binding energy of C $1s$ for both PVC and polyaniline is very different. Subsequently, we have chosen to use the Cl $2p_{3/2}$ (200.6 eV) or Cl $2p_{1/2}$ (202.2 eV) peak from PVC to calibrate all our spectra since they were well defined for all samples after peak fitting. Figure I-1 illustrates the peak fitting obtained for a CMX P1-0.75 sample. The corresponding peak parameters are given in Table I-1.

The deconvoluted S $2p$ peaks for CMX and CMX P1-1 membranes are represented in Figure I-2 and the corresponding peak fitting parameters are given in Table I-2. This curve-fitting was done to determine the binding energy of each peak.

Figure I-3 illustrates the scanning electron micrographs obtained for a CMX P1-1, CMX P1-10 and CMX membranes. A smoother surface is found at the surface of the membrane for which PANI degradation occurs. This surface is similar to the one obtained for an unmodified CMX membrane.

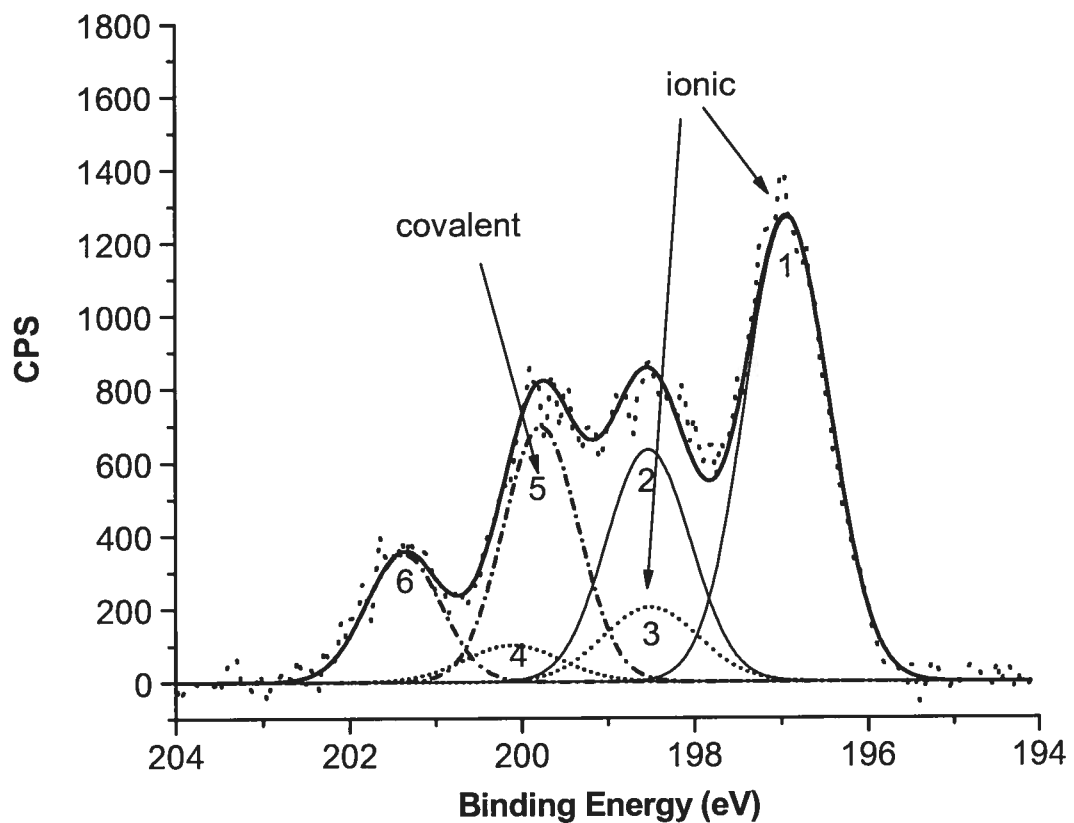


Figure I-1. Deconvoluted Cl $2p$ core-level spectrum for a CMX P1-0.75 composite membrane: experimental (•••) and fitting (—) curves. The arrows point at the $2p_{3/2}$ component of each pair of peaks. Refer to Table I-1 for fitting parameters.

Table I-1. Peak fitting parameters for the Cl $2p$ core-level spectrum of a CMX-P1-0.75 composite membrane (Figure I-1).

| Peak # | | Center (eV) | FWHM (eV) | Area (CPS*eV) |
|--------|------------------------|-------------|-----------|---------------|
| 1 | Cl $2p_{3/2}$ ionic | 197.9 | 1.1 | 1547 |
| 2 | Cl $2p_{1/2}$ ionic | 199.3 | 1.1 | 773 |
| 3 | Cl $2p_{3/2}$ ionic | 199.3 | 1.3 | 282 |
| 4 | Cl $2p_{1/2}$ ionic | 200.9 | 1.3 | 141 |
| 5 | Cl $2p_{3/2}$ covalent | 200.6 | 1.0 | 766 |
| 6 | Cl $2p_{1/2}$ covalent | 202.2 | 1.0 | 383 |

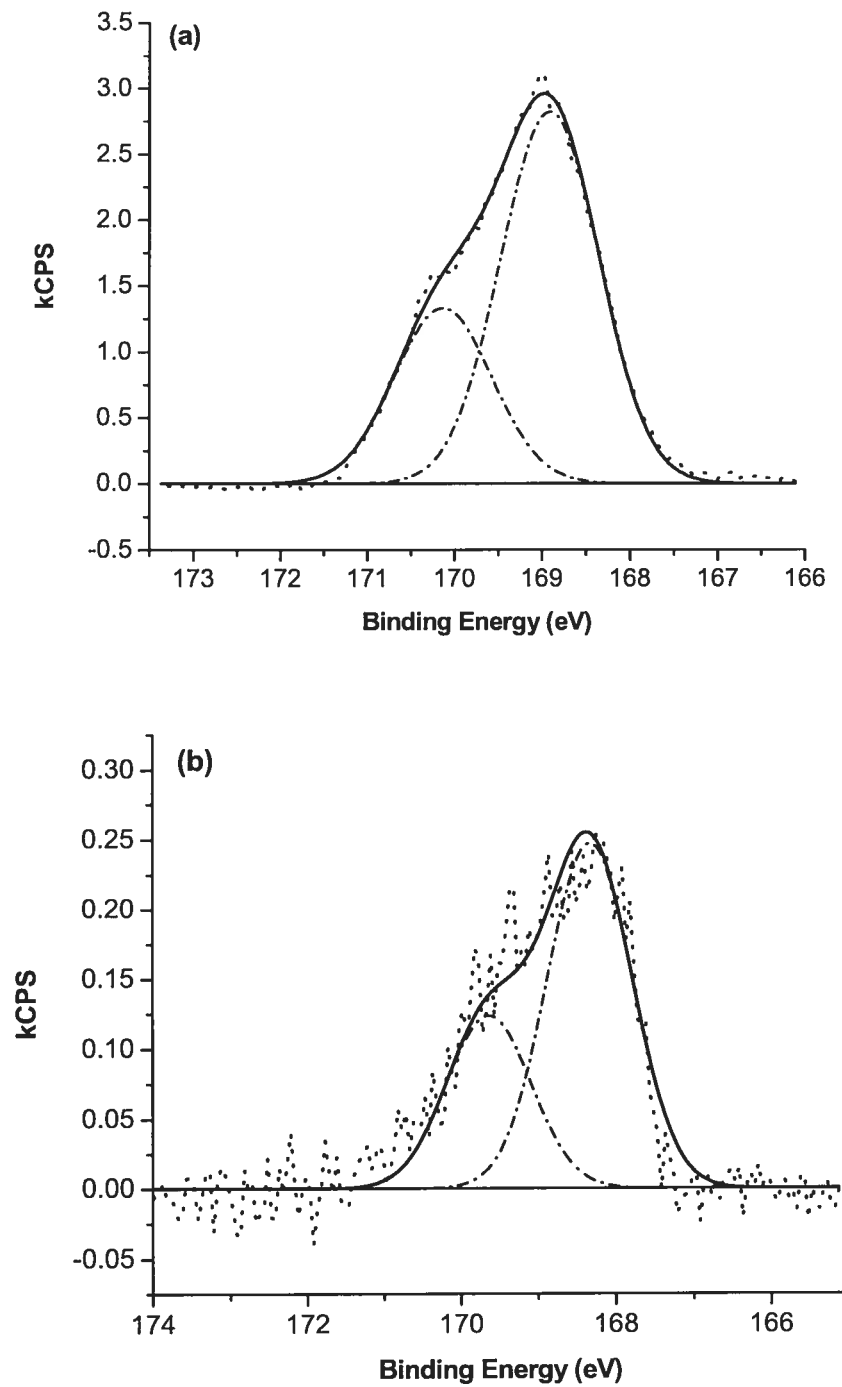


Figure I-2. Deconvoluted S 2p core-level spectrum for a CMX (a) and a CMX P1-1 (b) membrane: experimental (•••) and fitting (—) curves. Refer to Table I-2 for fitting parameters.

Table I-2. Peak fitting parameters for the S $2p$ core-level spectrum of a CMX and a CMX P1-1 composite membrane (Figure I-2).

| | | Center (eV) | FWHM (eV) | Area (kCPS*eV) |
|----------|--------------|-------------|-----------|-------------------|
| CMX | S $2p_{3/2}$ | 168.9 | 1.3 | 3.040 |
| | S $2p_{1/2}$ | 170.1 | 1.3 | 1.422 |
| CMX P1-1 | S $2p_{3/2}$ | 168.3 | 1.3 | 0.259 |
| | S $2p_{1/2}$ | 169.6 | 1.3 | 0.128 |

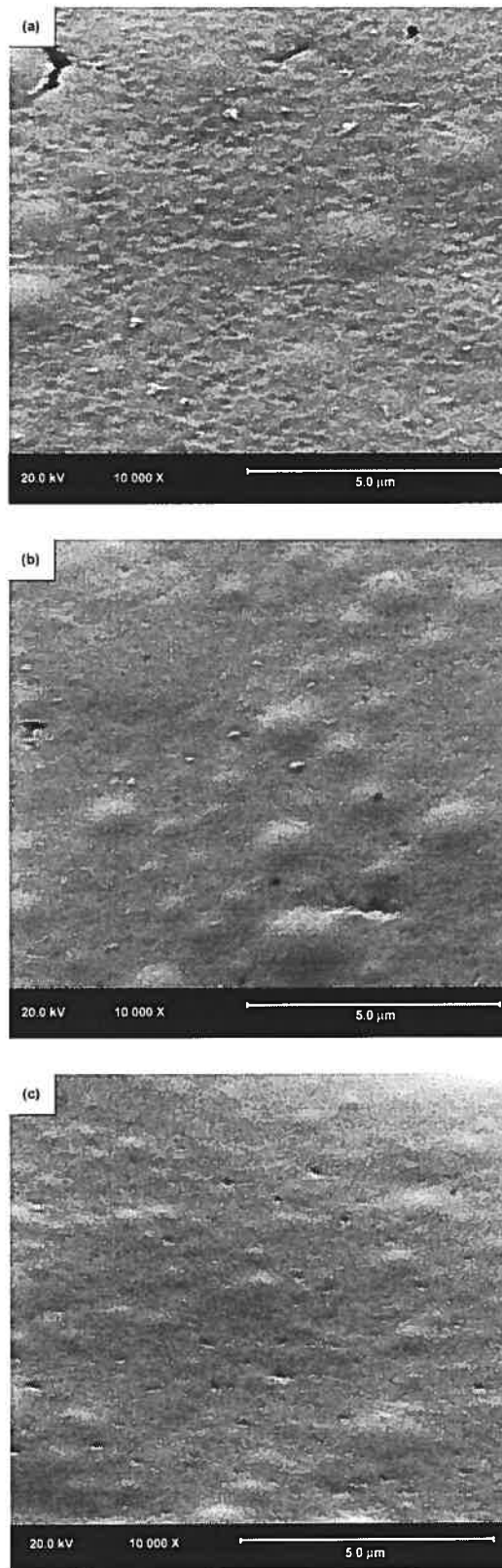


Figure I-3. Scanning electron micrographs of a: (a) CMX P1-1, (b) CMX P1-10 and (c) bare CMX membranes.

Annexe II

Matériel supplémentaire au chapitre 7

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Supporting Information

Characterization and Transport Properties of Nafion/Polyaniline Composite Membranes

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In the first result sub-section entitled “Chemical Polymerization of Aniline on Nafion membranes”, the description of the Nafion-PANI composite membranes prepared under different experimental conditions was given. The pictures of these composite membranes are presented here. Figure S1 (a) illustrates that the membrane obtained after 1 h oxidation using a 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidant solution (Naf P1-1-0.1) is green and slightly transparent and not totally homogeneous over the modified area. After 2 h oxidation using the same solution, the composite membrane becomes completely opaque. The membrane prepared using 1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 1 h oxidation time (Naf P1-1-1) is completely opaque. However, as opposed to Naf P1-2-0.1, a pink color appears around the modified area after over 24 h of storage in 1 M HCl or 1 M H_2SO_4 solution. The pink color is indicative of the presence of PANI oligomers.

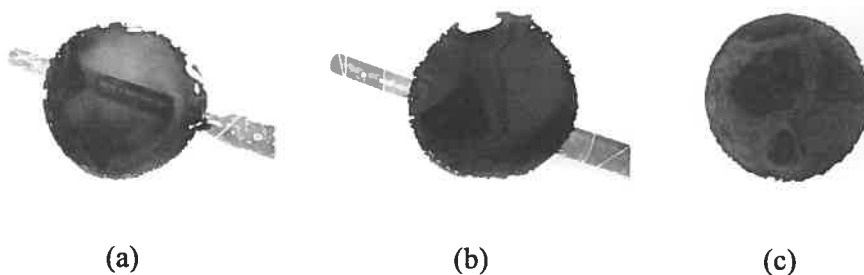


Figure II-1. Pictures of Nafion-PANI composite membranes prepared under different polymerization conditions: (a) Naf P1-1-0.1, (b) Naf P1-2-0.1 and (c) Naf P1-1-1. Membranes were conditioned in 1 M HCl for at least 24 h. A marker pen was placed under the membrane to show the degree of transparency of the composite membranes.

Annexe III

Liste des publications et contribution des co-auteurs

Articles publiés (*inclus dans la thèse)

1. *Tan, S., Viau, V., Cugnod, D. et Bélanger, D., Chemical Modification of a Sulfonated Membrane with a Cationic Polyaniline Layer to Improve its Permselectivity. *Electrochem. Solid-State Lett.* (2002) 5, E55-E58.
2. *Tan, S., Laforgue, A. et Bélanger, D., *Characterization of a Cation-Exchange/Polyaniline Composite Membrane*. *Langmuir* (2003) 19, 744-751.
3. Tan, S., Laforgue, A. et Bélanger, D. Improving the Permselectivity of Commercial Cation-Exchange Membranes for Electrodialysis Applications dans *Advanced Materials for Membrane Separations*, ACS Symposium Series, no. 876, American Chemical Society, 2004, pp. 311-323.
4. *Tan, S., Tieu, J.H. et Bélanger, D., *Chemical Polymerization of Aniline on a Poly(Styrene Sulfonic Acid) Membrane: Controlling the Polymerization Site Using Different Oxidants*. *J. Phys. Chem. B* (2005) 109, 14085-14092.
5. *Tan, S. et Bélanger, D., *Characterization and Transport Properties of Nafion/Polyaniline Composite Membranes*. *J. Phys. Chem. B* (2005) sous presse.

Contribution des co-auteurs

Il est à noter que j'ai rédigé et réalisé toutes les expériences décrites dans tous les articles inclus dans la thèse à l'exception des mesures par voltammétrie cyclique (Figure 4.2) effectuées par Dr. Alexis Laforgue, des images SEM enregistrées par M. Raymond Mineau et des spectres XPS, enregistrés par Prof. Daniel Bélanger. Cependant, j'ai personnellement traité et interprété les résultats de SEM et XPS. Pour l'article #1, Mme Valérie Viau et Mme Daphné Cugnod, deux stagiaires de premier cycle, ont réalisé des essais préliminaires menant aux résultats présentés dans cet article. Pour l'article #3, en plus des expériences de voltammétrie cyclique, Dr. Laforgue a contribué aux discussions et à la correction de l'article. Pour l'article #4, Mme Jacqueline Tieu était une étudiante de premier cycle ayant effectué un stage de fin de baccalauréat sous ma supervision et celle du Prof. Daniel Bélanger. Elle a effectué les études préliminaires menant aux travaux présentés dans cet article.