



# Synthesis and characterization of commercial cation exchange membranes modified electrochemically by polypyrrole: Effect of synthesis conditions on the transport properties



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## ABSTRACT

Herein, we report the galvanostatic modification of a commercial cation exchange membrane CMX by polypyrrole (Ppy). The presence of Ppy in the cation exchange membrane (CEM) was confirmed by cyclic voltammetry, stereo microscopy, fourier transform infrared spectroscopy, scanning electron microscopy, and energy dispersive X-ray. Ppy was present both on the membrane surface and inside the pores. The quantity of Ppy in CEM, compactness of Ppy, and the charges on Ppy (negative or positive) were controlled effectively by changing the electrosynthesis conditions. The permeability and water content of the modified membranes obtained under different conditions were investigated. The transport properties of the modified CEMs were evaluated qualitatively using polarization curves and quantitatively by chronopotentiometry. NaCl and MgCl<sub>2</sub> solutions ranging in concentrations from 5 mM to 0.1 M were used for testing the selectivity. The presence of Ppy in the membranes decreased the transport number of Na and Mg, and the reduction in transport number was more significant for Mg.

## 1. Introduction

Concentration of electrolyte solutions by electrodialysis is a significant physicochemical wastewater remediation technique due to its high performance over separation rates and low demand for chemicals during operation [1–2]. Electrodialysis is generally used for treating solutions containing two or more ions, as in the case of desalination of water [3], or waste from metallurgy and surface treatments [4]. In some cases, a particular ion might need to be removed from the effluent. Therefore, the selectivity of the ion-exchange membrane used is very important, and several approaches have been developed to improve this aspect [5,6]. Modification of ion-exchange membranes by intrinsically conducting polymers (ICPs) is one of the methods used to discriminate between species of different sizes and same charge present in an effluent [7–16]. In fact, the presence of ICPs in ion-exchange membranes decreases the permeation of divalent cations [16]. ICPs can improve selectivity for different reasons. The pores of the membrane modified with ICPs could be smaller than those of the untreated membrane, which makes the passage of bulkier ions difficult [9]. Additionally, ICPs can alter the hydrophilic character of the membrane [9], resulting in strong interaction of ions with the positive charges of

the ICPs [7,8,10–12]. The porosity [17,18], hydrophilicity [19], and amount of charge [20] of the ICPs can be modulated by changing the conditions of polymerization, and this can be carried out chemically or electrochemically. Electrochemical polymerization presents significant advantages over chemical synthesis, as there is no need for an oxidizing agent, and fine control of the initiation and termination reaction can be achieved [20,21]. However, there have been few reports of electrochemical methods used [12,13] for the modification of ion-exchange membranes. On the other hand, modification has been carried out using two ICPs: polyaniline (PANI) [7–13] and, to a lesser extent, polypyrrole (Ppy) [14–16]. To the best of our knowledge, there have been no reports of commercial membranes modified electrochemically by Ppy.

In this work, we present the electrochemical modification of a commercial cation exchange membrane by polypyrrole and its characterization. The porosity and charges were modulated by the electrosynthesis conditions and the selectivity of these membranes was evaluated by chronopotentiometry using NaCl and MgCl<sub>2</sub> solutions of various concentrations. Films with the same amount of charge and different compactness were obtained using water and acetonitrile as solvents during electrosynthesis. The amount of Ppy was varied by changing the time of electrosynthesis. The charge was modulated by

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**Table 1**  
Properties of the commercial membranes used in this work.

	Fixed charge	Electric resistance/ $\Omega\text{cm}^{-2}$	Pressure resistance/MPa	Thickness/mm	Exchange capacity/ $\text{meqg}^{-1}$	Transport number
CMX	$-\text{SO}_3^-$	1.80–3.80	$\geq 0.40$	0.14–0.20	1.50–1.80	$\text{K}^+ / 0.96$
AFN	$-\text{NR}_3^+$	0.3–1.0	$\geq 0.25$	0.13–0.18	2.0–3.5	$\text{NO}_3^- / 0.93$

changing the degree of oxidation of Ppy, as the functional groups of overoxidized Ppy [22,23] are different from those of untreated Ppy.

## 2. Materials and methods

### 2.1. Materials

The CMX cation exchange and AFN anion exchange membranes used were supplied by ASTOM Corp., Japan. Table 1 lists the principal properties of these membranes.

### 2.2. Electrochemical modification of membranes

Pyrrole (Sigma-Aldrich) was purified prior to use by passing through a micro-column constructed from a Pasteur pipette and silica. This procedure was repeated several times until a colorless liquid was obtained. The aqueous solutions were prepared using deionized water (18.8 M $\Omega\text{cm}$ ), and the solutions were deoxygenated by purging with nitrogen gas. Following this, a nitrogen atmosphere was maintained in the solutions during each run.

The experimental montage for electrochemical polymerization was carried out according to Montes et al. [13]. Briefly, a typical three-electrode cell was used, consisting of a commercial membrane adhered to a carbon paste electrode (2.8153 cm<sup>2</sup>) as working electrode, platinum spiral as counter electrode, and Ag/AgCl/NaCl 3 M (BASi) as the reference electrode. The carbon paste electrode was prepared by thoroughly mixing graphite powder (Alfa-Aesar) and Nujol (Alfa-Aesar) in proportion 60:40 w/w, and packing the resulting paste into a plastic 20 mL syringe in which a piece of copper wire was wound to produce the electrical contact. The membranes were pretreated by immersing in the support electrolyte solution for 1 h.

To perform the electrochemical polymerization and characterization of Ppy, a potentiostat/galvanostat (BAS Epsilon) controlled by software (Epsilon-EC, version 1.31.65 NT) was used.

Electrochemical deposition was carried out in the galvanostatic mode, and the constant current density used was 3.55 mAcm<sup>-2</sup>. The synthesis time was varied between 30 and 840 s, resulting in deposits with varying amounts of Ppy. The working solution for electrodeposition was composed of pyrrole (0.01 M) and LiClO<sub>4</sub> (Aldrich, 0.1 M), with water and/or acetonitrile (Fermont) as solvents. After deposition, the membrane was detached from the surface of the carbon paste electrode, and sonicated in chloroform to eliminate residues of carbon paste and oligomers of pyrrole. Following this, the membranes were used in chronopotentiometric tests or for the measurement of polarization curves and therefore the Ppy used was oxidized.

For cyclic voltammetry studies, the modified membranes were attached to the surface of the carbon paste electrodes, and scanned from -100 to 700 mV at 100 mVs<sup>-1</sup> in a solution containing only the support electrolyte. The charge of each film was obtained by the area under the curve of the voltammogram.

The deposits of Ppy were overoxidized by imposing a constant potential of 1200 mV for 5 min in a working solution of LiClO<sub>4</sub> (0.1 M).

### 2.3. Characterization of the modified membranes

Scanning electron microscopy (SEM) studies were carried out using a Helios Nano Lab DualBeam 600 instrument, equipped with an energy dispersive X-ray spectroscopy (EDX) system operating at 5 kV. Samples

were mounted on a disk and sputter-coated with a thin layer of gold. For micrographs transversal of membranes, membranes were frozen using liquid nitrogen and divided by a cutter. Stereo microscope used was an Olympus SZX16.

For water content test the membranes were immersed in distilled water for 24 h at room temperature (27 °C), the surface wiped with filter paper, and weighed with an analytical balance (Hinotek DHG-9145A). The wet membranes were dried at a fixed temperature (50 °C) until a constant weight was obtained (approximately 4 h). The following equation was used for the calculation of water content:

$$\text{water content \%} = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \right) \times 100 \quad (1)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the membrane at the equilibrium swelling and dry state, respectively.

The water vapor permeability test of the membranes was carried out using cylindrical penny cups of area 1.7671 cm<sup>2</sup>. The cups, each containing 5 g of water, were covered by the membranes (2.8353 cm<sup>2</sup>) and closely fixed by Parafilm. The water vapor permeability was determined by the loss of water/h through the membrane.

Reflectance infrared spectra were recorded using a Nexus series 470 instrument. Typically, 2 scans were recorded in the range 5000–400 cm<sup>-1</sup>, with a resolution of 1 cm<sup>-1</sup>. Fourier transform infrared spectroscopy (FTIR) data were collected using the Bomem Grams/386 software for Windows (Version 3.01B, level II, 1991–1994).

### 2.4. Current-voltage polarization and chronopotentiometric curves

Current-voltage and chronopotentiometric curves were recorded using an acrylic cell, fabricated in-house for the purpose. The cell contains four compartments (Fig. 1) with separating walls, and have a circular hole (diameter: 1 cm) in the geometric center, into which the membranes were clamped. The outer well contains the auxiliary membranes, CMX and AFN, while the membrane under study was placed in the central well. The face of membrane in contact with the solution during electrochemical modification was on the anode side. Two Pt spirals were placed in the outer compartments and used as the working electrodes. The chronopotentiometric curves were obtained using the same cell by the application of current between these electrodes using a galvanostat fabricated in-house. The resultant voltage was measured using a digital multimeter (LINI-T) connected to two Ag/AgCl/NaCl 3 M (BAS) electrodes, which were coupled with capillaries brought to the surface of the membrane under study. Data were collected using the program of the multimeter. The same configuration was used to obtain the polarization curves; however, in this case, a potential was applied between the Pt electrodes, and the resultant current and membrane potential were individually measured by a multimeter. The data were recorded manually. Solutions of NaCl (Fermont) and MgCl<sub>2</sub> (J. T. Backer) were used for these studies.

## 3. Results and discussion

### 3.1. Synthesis and electrochemical characterization of the modified membranes

The membranes were modified electrochemically using the method reported earlier [13], in which the nonconducting membrane was adhered to a carbon paste electrode (CPE), and the ensemble formed

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