Development of bivalent cation selective ion exchange membranes by varying molecular weight of polyaniline

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ABSTRACT

A novel hybrid cation exchange membrane (CEM) composed of a blend of polyvinylidene fluoride (PVDF), sulfonated PVDF(S-PVDF) and doped polyaniline (PANi) as additive was prepared. PANi was synthesized with different molecular weights to optimize the performance of membranes for water softening. The membrane properties such as thermal behavior, membrane structure, membrane morphology and miscibility, ion exchange capacity (IEC), permselectivity, water uptake, contact angle, cell resistivity, current efficiency and electrodialysis (ED) performance were evaluated. Addition of doped PANi increased the bivalent selectivity of the cation exchange membrane. The highest bivalent selectivity and best removal of Ca^{2+} and Mg^{2+} were achieved for PANi with $M_w \approx 45{,}000\,g\,mol^{-1}$ and polydispersity index (PDI) ≈ 3.2.

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1. Introduction

Electrodialysis (ED) is a separation technology that has been used for over 50 years for the production of potable water from brackish water [1]. This process is also utilized for many other applications based on selective extraction of cations such as sodium chloride (NaCl) concentration for the chlor-alkali industry [2], removal of specific cations from industrial wastewater treatment [3] and acid effluents [4], hydrometallurgy [5], water softening [6], reverse electrodialysis (RED) [7] etc.

The electrochemical properties and selectivity of ion exchange membranes play a key role in the performance of the ED process [8].

A novel cation exchange membrane (CEM) based on sulfonated polyvinylidene fluoride (S-PVDF) blended with polyvinylidene fluoride (PVDF) has recently been developed [9]. It was found that for different percentages of S-PVDF, the resulting membranes are bivalent selective.

To develop the bivalent selectivity of membranes and using these membranes in water softening (requiring the reduction of Mg^{2+} and Ca^{2+} concentrations in water [10]), polyaniline (PANi) was selected to blend with the main composition. PANi is an interesting electrically conducting polymer featuring easy synthesis and chemical stability [11]. Other advantages of PANi include the ease of doping/dedoping with acid/base which allows keeping the ion exchange capacity of the membrane as high as possible, and the solubility of PANi in N-methyl pyrrolidone (NMP), which is also the solvent for PVDF/S-PVDF solution blending.

It was found that camphorsulfonic acid (CSA) is an organic dopant that increases the solubility of PANi in the NMP solvent [12] and its nature is more hydrophilic than other organic dopants which provides more bivalent selectivity [13].

F. D. R. Amado et al. [14] used PU/PANi composite membrane with CSA and para toluene sulfonic acid as dopants for zinc extraction from zinc acid solution, but with a few study on electrochemical properties of membranes and without estimation of cation selectivity.

Since molecular weight and molecular weight distribution are the key features of any polymer and markedly affect the physical and mechanical properties of the films or fibers made from the polymer [15–17], and to adapt the electrochemical properties of composite membranes, PANi was synthesized in different molecular weight by variation of the synthetic conditions such as temperature and reaction time [18,19]. The influence of PANi molecular weight on the composite membranes properties and consequently on their performance was investigated to achieve the highest bivalent flux and selectivity.

2. Experimental

2.1. Materials

PVDF (grade Solef® 6020) was purchased from Solvay, 1,2-dichloroethane (≥99% pure) from Merck, N-methyl-2-pyrrolidone

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(NMP) ($\geq$99.5% pure) and aniline (99.8% pure) from Acros, ammonium peroxodisulfate (APS) (98% pure) from Chem-Lab and chlorosulfonic acid ($\geq$98.0% pure) from Fluka. Camphorsulfonic acid (CSA) and 4-methylpiperidine (4-MP) 96% were acquired from Sigma-Aldrich. Hydrochloric acid (HCl) 1 N, sodium hydroxide (NaOH) (beads with 97% purity) and ammonia 32% (NH_4OH) were purchased from VWR chemicals. Anion exchange membranes (homogenous fumasep® FAB) was acquired from Fumatech.

2.2. Synthesis of sulfonated PVDF (S-PVDF)

The sulfonation of PVDF was carried out according to previously reported procedures [9,13]. 10 g of PVDF powder was added to 50 ml chlorosulfonic acid and mixed at a temperature of 80 °C for 45 min. The product was precipitated first in 1,2-dichloroethane and then in deionized water. The resulting precipitate was filtered and washed with 1,2-dichloroethane and deionized water. The obtained S-PVDF was then dried in a vacuum oven at 50 °C for 1 h.

2.3. Synthesis of PANi with different molecular weights

Emulsion polymerization of aniline was carried out by adapting the procedure described earlier [20]. In a typical polymerization, 0.06 mol of HCl and 0.06 mol of aniline are dissolved in 200 ml of deionized water under stirring in a bath maintained at a constant temperature. Different temperatures were used to obtain different molecular weights: −10 °C, 0 °C and 20 °C. For 0 °C, 2.1 g LiCl (0.05 mol) and for −10 °C, 4.2 g LiCl (0.1 mol) was added to prevent freezing of water. After appropriate stirring, 13.69 g (0.06 mol) of APS as an initiator dissolved in 60 ml of water was drop-wise poured into the polymerization bath for a period of 0.5 h, and the reaction mixture was left stirring for 2 h. At 0 °C another PANi sample was synthesized by mixing for 16 h to evaluate the role of reaction time on the molecular weight. The resulting precipitate was filtered and washed with deionized water until the filtrate was colorless (to nutrient pH). Then, the resulting PANi, obtained as an emeraldine salt (ES), was stirred in 1 M solution of ammonium hydroxide at room temperature for 1 h to have it completely converted to its emeraldine base (EB) form. Upon filtering and drying under dynamic vacuum in an oven at 55 °C for 12 h, the base form of PANi was obtained as a blue powder. In Table 1, the different synthesized PANi compounds are defined according to the applied synthesis conditions.

2.3.1. Synthesis of S-PVDF/PVDF/PANi composite membrane

S-PVDF/PVDF/PANi membranes were prepared by performing co-dissolution in NMP. A 10 % wt solution of S-PVDF in NMP and a 10% wt solution of PVDF in NMP were prepared separately. 10 %wt PANi (with different molecular weights) solutions were made in NMP/4-MP solution. 4-MP was used as anti-gel in the ratio of 1:2 with respect to the aniline monomer.

The S-PVDF solution was first added to the PVDF solution under stirring in an appropriate amount to form S-PVDF/PVDF blend with an S-PVDF share of 50%. Then the PANi solution with an appropriate amount of CSA (1.25 g CSA per 1 g PANi) as doping agent was added to this blend to obtain a PANi share of 5% wt. The

blended solution was casted on a glass plate with a casting knife and then dried in a dynamic vacuum oven at 60 °C overnight. Then, the synthesized membrane was peeled off by immersion of the glass plate in water and was immersed in a 1 M NaCl solution for at least 24 h to reach equilibrium conditions.

Each membrane was named according to the PANi type that was used in the composite membrane. The base membrane without any PANi was named S-50.

2.4. Characterization techniques

2.4.1. Molecular weight

Gel permeation chromatography (GPC) was used to estimate the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) as a measure of the width of the molecular weight distribution of synthesized PANis.

Molecular masses were measured on a GPC system using a Waters 610 fluid pump, Waters 2414 RI detector, Merck Hitachi column oven L-7300, Waters 717 Plus autosampler and with set of columns PSS GRAM (10 μm 8.0 × 50 mm, 30 Å, 10 μm 8.0 × 300 mm, 1000 Å, 10 μm 8.0 × 300 mm). N,N-dimethylacetamide (DMA) containing LiBr was used as eluent with a flow rate fixed at 1 ml min^{-1} and a temperature of 40 °C, with poly(methylmethacrylate) standards.

2.4.2. Thermogravimetric analysis (TGA)

The doping amount of PANi and thermal behavior of composite membranes were evaluated by thermogravimetric analysis (TGA) in the range of 20–750 °C. TGA test was carried out using a Netzsch (STA 409 PC Luxx® model) system with a controlled heating rate 10 °C/min in nitrogen atmosphere.

2.4.3. Membrane structure

The compactness and crystallinity of membranes were evaluated by X-ray diffraction (XRD). The XRD studies were performed on a Philips X-ray diffractometer (PW1830 model) using a CuKα radiation source (1.542 Å). The scan range (2θ) was 5–50° at a scan rate of 2° min^{-1}.

2.4.4. Morphology and miscibility

A scanning electron microscope (SEM) ((Philips XL30 FEG, the Netherlands) was used to visualize the morphology and miscibility of the membranes. SEM images were taken in high vacuum condition at 20 kV.

2.4.5. Water uptake

All membranes were dried in vacuum at 60 °C for 4 h before testing. The sample membranes were soaked in deionized water at room temperature for 24 h. The water remaining on the surface of the wetted membrane was removed using tissue paper before weighing. The water uptake was calculated by:

$$Uptake = [(w_{wet} - w_{dry})/w_{dry}] \times 100\% \qquad (1)$$

Where w_{wet} and w_{dry} were the masses of dried and wet samples, respectively.

Table 1
Synthesis condition and molecular weight data of different PANi samples

PANi name	Temperature (°C)	Reaction time (h)	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI
B-10	-10	2	45374	14233	3.19
B0	0	2	47275	17017	2.78
B016	0	16	28037	7932	3.53
B20	20	2	12516	4794	2.61