



Preparation, characterization and thermal degradation studies of bi-functional cation-exchange membranes



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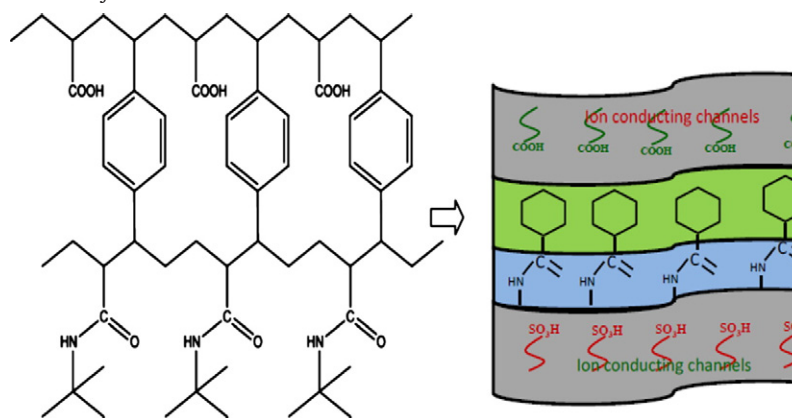
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HIGHLIGHTS

- Preparation of cross-linked bi-functionalized copolymer by radical polymerization
- Cation-exchange membrane showed high bound water content.
- Study on trade-off behavior between membrane stabilities and conductivity
- Thermal stable cation-exchange membrane for electro dialysis

GRAPHICAL ABSTRACT

Thermal stable bi-functionalized CEM with high bound water content by radical polymerization/cross-linking for electro dialysis.



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ABSTRACT

Cross-linked divinylbenzene (DVB) based bi-functional copolymer (BFC) was synthesized using acrylic acid and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) by free radical copolymerisation reaction. Simple solution casting technique was used to fabricate the bi-functional cation-exchange membranes using polyvinyl alcohol (PVA) as plasticizer. To deliberate the structural and morphological analyses and assess the density of functional groups, state of water, and conductivity of developed membranes, physicochemical characterizations were carried out. Well optimized PVA/BFC-70 membrane showed high bound water content (3.60%) with high membrane conductivity ($3.67 \times 10^{-2} \text{ S cm}^{-1}$) and ion-exchange capacity ($1.30 \text{ mequiv g}^{-1}$). The reported CEM, especially PVA/BFC-70, was assessed for the electrochemical applications.

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1. Introduction

The ion-exchange membranes (IEMs) were widely studied for ionic separation processes including food, drug, chemical and water industries

[1–8]. Particularly, for water desalination and ionic separation, IEM should exhibit high ionic conductivity and permselectivity along with good mechanical, thermal and chemical stabilities [1,6,9]. Selection of polymeric matrix, density of functional groups, permselectivity and other tunable properties were utilized as strategic tools to achieve the efficient IEM. Generally, cation-exchange membranes (CEMs) are prepared by sulphonation of polymer [1,5,10]. To date, poly(perfluorosulphonic acid) (Nafion) [1], sulphonated polystyrene, sulphonated polysulfone [11], poly-(ether ether ketones) [12], polyimides [13], poly(phenylquinoxaline) [14], polyphenylenes [15], polybenzimidazoles [16], etc. were proposed as potential CEM. To achieve good conductivity, ion-exchange capacity and permselectivity, high degree of sulphonation was required, but dissolution of sulphonated polymers requires controlled sulphonation up to desired extent [5]. Further, dimensional instability under harassed oxidative conditions at relatively high temperature also limits the high temperature applicability of these CEMs.

Water soluble polymers were also used for the preparation of CEMs, because membrane charge density and stability can be easily controlled by incorporating ion-exchange material. Numerous CEMs were reported based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), because of their high conductivity due to high molality of $-SO_3H$ groups [17–21]. But, these membranes based on water soluble polymers suffered with excess swelling and hydrolytic instability, while maintaining high conductivity and introducing monomers with weak acidic group ($-COOH$) such as acrylic acid (AA) [17,22,23]. To achieve the good stability, cross-linking is an attractive method, and high degree of functionalization may be obtained without impairing mechanical instability and other properties [24,25]. In addition, cross-linked CEM grafted with weak and strong acidic groups ($-COOH$ and $-SO_3H$, respectively) seems to be interesting for high degree of stabilities. Bi-functionalized CEM composed of well defined hydrophilic and hydrophobic regions is expected to exhibit phase separation, stability with ion conducting channels spaced by hydrophobic regions. Particularly, high water retention ability (high bound water content due to plenty of functional groups), which is essential to achieve high performance (conductivity) and durability without any deterioration due to dehydration, would be the attractive features for bi-functionalized CEMs [26,27].

Herein, bi-functionalized copolymer (BFC) based CEM was prepared by AMPS, AA and divinyl benzene (DVB) using radical polymerization and cross-linking. Poly(vinyl alcohol) (PVA), a well-known semi-crystalline polymer was used as plasticizer because of its chemical cross-linkable nature with a suitable cross-linking agent. BFC content in the membrane matrix controls the stability and electrochemical properties of the developed composite CEM. Developed CEMs with BFC content were characterized for their performance in water desalination at different temperatures by electro dialysis.

2. Experimental section

2.1. Materials

2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and divinylbenzene (DVB) were obtained from Sigma-Aldrich Chemicals and used as received. Polyvinyl alcohol (PVA), acrylic acid (AA), dimethyl sulphoxide (DMSO), benzoyl peroxide (BPO), formaldehyde, H_2SO_4 , NaCl, and Na_2SO_4 of AR grade were received from S.D. Fine Chemicals, India. Double distilled water was used for all purposes.

2.2. Synthesis of BFC copolymer

In a typical procedure, three-neck round bottom flask (100 ml) was charged with AA (0.09 mol), AMPS (0.21 mol), DVB (0.05 mol), and DMSO (14 ml) and stirred followed by addition of BPO (small amount) to initiate the copolymerization reaction. The reaction temperature was kept at 60 °C for 6 h under N_2 atmosphere to complete the copolymerization reaction. The reaction mixture was precipitated in an excess of

acetone, filtered, washed with acetone, and dried at 60 °C for 12 h to obtain BFC copolymer. Chemical structure of the prepared BFC was confirmed by FTIR studies.

2.3. Membrane preparation

PVA solution (10 wt.%) was in water under stirred condition. The pre-estimated amount of BFC was added under stirring at room temperature for 6 h. Resultant homogeneous mixture was transparent with highly viscous. After removal of air under vacuum, solution was transformed into thin film of desired thickness on a clean glass plate. The membranes were dried under IR lamps and cured at 60 °C under vacuum for 12 h. Thus obtained flexible brownish, and transparent membrane was peeled off for cross-linking with a formal solution ($HCHO + H_2SO_4$) for 3 h at 60 °C. The prepared membranes were designated as PVA/BFC-X, where X denotes 0, 30, 50, and 70 wt.% of BFC in the membrane forming material.

2.4. Instrumental and physicochemical characterization of the membranes

Detailed instrumental analysis such as infrared spectra, TEM, optical image, TGA, DSC and DMA studies is included in Section S1 (Supplementary data). Bound water content was estimated from weight loss percentage obtained from TGA by sample heating between 100 and 150 °C with $10\text{ }^\circ\text{C min}^{-1}$ rate under nitrogen atmosphere.

2.5. Water uptake, ion-exchange capacity (IEC), water retention and membrane stability studies

Detailed procedures for the determination of water uptake and number of water molecules associated per ionic sites (λ) are included in Section S2 (Supplementary data). IEC was measured by the back-titration method, while water retention ability of membrane was analysed by TGA study (Section S2, Supplementary data). Procedures for studying oxidative and hydrolytic stabilities of the composite membranes are included in Section S3 (Supplementary data).

2.6. Membrane conductivity, counter-ion transport number and permselectivity measurements

Detailed procedure for ionic conductivity measurement has been included in Section S4 (Supplementary data). Counter ion transport number in the membrane phase was obtained by the Hittorf method [28]. Detailed procedures adopted for the measurement of counter-ion transport and permselectivity are also included in Section S4 Supplementary data.

2.7. Electrodialytic performance of composite CEMs

A laboratory-scale electro dialysis unit was fabricated with 4 cell pairs of prepared BFC-70 membranes and anion-exchange membrane (AEM) (ASV supplied by Selemion, Japan) with 80 cm^2 effective membrane area (Fig. S1, Supplementary data). Properties of AEM are included in (Table S1, Supplementary data). The parallel-cum-series flow arrangement was used to monitor flow stream of each compartments. Na_2SO_4 solution (0.10 M) was recirculated in both electrode wash (EW) compartments, separately. Initially, NaCl solution of known concentration (5000 ppm) and volume was fed into dilute compartment (DC), while distilled water was fed into concentrate compartment (CC). Peristaltic pumps were used to feed the solutions (500 cm^3) in a recirculation mode into the respective compartments with constant flow rate ($0.012\text{ m}^3\text{ h}^{-1}$) to maintain the turbulence. Precious metal oxide coated titanium sheets (TiO_2 sheet coated with a triple precious metal oxide (titanium–ruthenium–platinum), of 6.0 μm thickness, and $8.3 \times 10^{-3}\text{ m}^2$ effective area) obtained from Titanium Tantalum Products (TITAN, Chennai, India) were used as the cathode and anode. A

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