



Bifunctionalized organic–inorganic charged nanocomposite membrane for pervaporation dehydration of ethanol

Bijay P. Tripathi, Mahendra Kumar, Arunima Saxena, Vinod K. Shahi *

Electro-Membrane Processes Division, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), GB Marg, Bhavnagar 364 002, Gujarat, India

ARTICLE INFO

Article history:

Received 14 November 2009

Accepted 11 February 2010

Available online 14 February 2010

Keywords:

Organic–inorganic nanocomposite

Modified chitosan

Pervaporation

Separation

Water–ethanol mixture

ABSTRACT

Chitosan was modified into *N-p*-carboxy benzyl chitosan (NCBC) by introducing an aromatic ring grafted with acidic –COOH group and highly stable and cross-linked nanostructured NCBC–silica composite membranes were prepared for pervaporation dehydration of water–ethanol mixture. These membranes were tailored to comprise three regions namely: hydrophobic region, highly charged region and selective region, in which weak acidic group (–COOH) was grafted at organic segment while strong acidic group (–SO₃H) was grafted at inorganic segment to achieve high stability and less swelling in water–ethanol mixture. Cross-linking density and NCBC–silica content in membrane matrix has been systematically optimized to control the nanostructure of the developed polymer matrix for studying the effects of molecular structure on the swelling, and PV performance. Among prepared membranes, nanocomposite membrane with 3 h cross-linking time and 90% (w/w) of NCBC–silica content (PCS-3-3) exhibited $1.66 \times 10^{-4} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cmHg}$ water permeability (P_w), while $1.35 \times 10^{-7} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cmHg}$ ethanol permeability (P_{EtOH}) of developed membrane and 1231 PV selectivity factor at 30 °C for separating water from 90% (w/w) ethanol mixture.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

Membrane technologies are promising separation method that has been used in industrial processes due to its easy operation, effective, energy saving and eco-friendly in nature. Pervaporation is a membrane based processes, which have been actively explored for the separation and purification of liquid mixtures especially aqueous–organic azeotropes [1–3]. Ethanol is a clean source of energy, produced by fermentation of biomass at low concentration, which must be concentrated before its industrial application. In general, a dilute aqueous solution of ethanol can be concentrated by distillation; however ethanol and water form an azeotrope mixture (95.6 wt.% ethanol) that cannot be separated by distillation. On the other hand, pervaporation can be applied to separate an azeotropic water/ethanol mixture.

Chitosan is a promising membrane material widely studied for PV separation due to their hydrophilicity, good film forming characteristics and excellent chemical-resistant properties [4–11]. However, swelling of the chitosan membrane in an aqueous solution, results in both an increase in solubility and diffusivity of alcohol, and consequently lowers the dehydration of ethanol–water mixture. For controlling membrane swelling, reports are available

including introduction of cross-linked structure to the membrane, blending of chitosan with other polymers, and developing organic–inorganic hybrid membranes [4–16]. Recently, sol–gel based organic–inorganic hybrid materials are reported to be the next generation of membrane forming material with high stabilities and reduced swelling properties because of controlled cross-linking and bond formation between organic and inorganic segments [4,6,17–25].

In our previous work, chitosan was modified into *N-p*-carboxy benzyl chitosan (NCBC) by introducing an aromatic ring grafted with carboxylic acid as the proton conducting group. Preparation procedure of highly conductive and stable organic–inorganic nanostructured NCBC–silica–poly(vinyl alcohol) (PVA), based proton exchange membrane (PEM) for direct methanol fuel cell (DMFC), by the sol–gel method in aqueous media was reported [26]. These PEMs were developed by cross-linking and designed to consist of weak proton conducting (–COOH) groups at organic segments and strong proton conducting (–SO₃H) groups at inorganic segments to achieve high degree of stabilities and hydrophilic region composed of highly charged and selectivity region. Developed membranes showed excellent thermal, chemical and mechanical stabilities along with high membrane conductivity ($5.31 \times 10^{-2} \text{ S cm}^{-1}$) and extremely low methanol permeability ($7.27 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), and found to be suitable for DMFC applications. Due to alcohol impervious nature of these membranes, we explored their spin-off application for pervaporation dehydration of ethanol.

* Corresponding author. Fax: +91 278 2567562/2566970.

E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).

In this manuscript we are reporting further studies for nanostructured NCBC–silica–poly(vinyl alcohol) (PVA) consisting of three regions (hydrophobic region, highly charged region and selective region) for efficient and highly selective dehydration of ethanol. These membranes offered superior PV performance over previously reported chitosan based membranes.

2. Experimental section

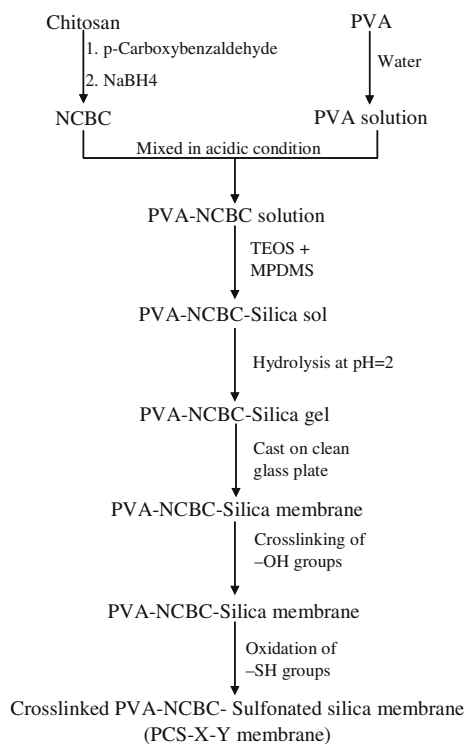
2.1. Materials

Deacetylated chitosan (100% deacetylated), 4-carboxy benzaldehyde, mercaptopropylmethyldimethoxysilane (MPDMS) and tetraethoxysilane (TEOS) were purchased from Sigma Aldrich Chemicals and used as received. Poly(vinyl alcohol) (PVA, MW: 125,000 degree of polymerization: 1700, degree of hydrolysis: 88%), ethanol, acetic acid, sodium borohydride, formaldehyde, hydrogen peroxide, etc. of AR grade were obtained from SD Fine Chemicals India, and used without any further purification. All other chemicals used were of AR grade from commercial sources. In all experiment double distilled water was used.

2.2. Modification of chitosan and membrane preparation

The method for the modification of chitosan into *N-p*-carboxy benzyl chitosan (NCBC) is based on the Michael condensation reaction. The detailed procedure for the modification of chitosan and preparation of hydrophilic bifunctionalized membranes has already been reported in our previous work [26]. In brief, procedure for the membrane preparation has been depicted in Scheme 1.

Obtained membranes were designated as PCS-X-Y, where X = 1, 2 and 3 designated as 50%, 70% and 90% (w/w) of NCBC–silica content in the membrane phase, and Y is the time of cross-linking (Y = a, b and c representing 1, 2, and 3 h). Thus nanocomposite membranes with varied NCBC–sulfonated silica content and



Scheme 1. Flow diagram of membrane preparation.

cross-linking time were prepared and tested for the dehydration of ethanol.

2.3. Characterization of nanocomposite membranes

The detailed characterization like ¹HNMR, FTIR, thermal and mechanical stability, surface morphology by SEM and TEM has already been reported in our previous research paper [26]. The cross-linking density (ρ) for the developed membranes was calculated from the procedure reported earlier [26]. The solvophilic nature of membrane surfaces was assessed by measuring contact angle using a DCAT21 Tensiometer (Dataphysics). The least count of used instrument was 0.0001° for the measurements of contact angle. Thickness of all prepared membranes was 150 μm . The contact angle (θ) was measured by dynamic Wilhelmy method. The rectangular shaped piece of membrane was moved at a constant rate of 52 $\mu\text{m/s}$ into the deionized water and pure ethanol and the force was monitored. After a certain depth, the movement was reversed and the sample was removed at the same rate.

Swelling properties of the developed membranes were determined by water uptake ϕ_w measurements while ion-exchange capacity (IEC; meq. g^{-1}) measurements were carried out by acid–base titrations as reported earlier [13,26,27].

ϕ_w data along with IEC values can be used with the advantage for the estimation of fixed charge concentration (X^m) in the membrane [(moles of ionic sites)/(unit volume of wet membrane)] by Eq. (1) [28].

$$X^m = \tau \times \text{IEC} \times \rho_d / \phi_w \quad (1)$$

where IEC is expressed in equivalents per gram of dry membrane, ρ_d is the density of dry membrane, and τ denotes membrane void porosity (volume of water within membrane per unit volume of wet membrane), defined as: $\tau = \phi_w / 1 + \phi_w$.

2.4. Pervaporation (PV) experiments

The PV experiments were carried out using the apparatus described in Fig. 1, under the following conditions: temperatures of feeding solutions, 30–50 °C; permeate side pressure, 1.0 cmHg. The effective membrane area was $4.07 \times 10^{-3} \text{ m}^2$. An aqueous solution of ethanol with varied v/v concentration was used as the feed solution. Permeate was collected in a tube at liquid nitrogen temperature. The compositions of the feed and permeate solution were determined using a digital refractometer (accuracy up to four digits, Mettler Toledo model No. RE-40D). During PV, permeabilities of individual components (ethanol and water) were deter-

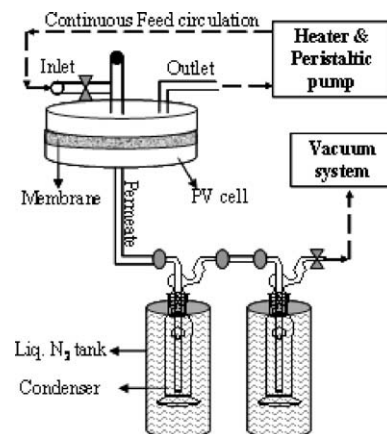


Fig. 1. Schematic diagram for PV experiments.

Download English Version:

<https://daneshyari.com/en/article/609296>

Download Persian Version:

<https://daneshyari.com/article/609296>

[Daneshyari.com](https://daneshyari.com)