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Preparation of organic–inorganic composite anion-exchange membranes via aqueous dispersion polymerization and their characterization

R.K. Nagarale, G.S. Gohil, Vinod K. Shahi [*], R. Rangarajan

Central Salt & Marine Chemicals Research Institute, Bhavnagar 364002 (Gujarat), India

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Abstract

Organic–inorganic composite membranes based on poly(vinyl alcohol)/SiO_2 were prepared via an aqueous dispersion polymerization route and anion-exchange groups were introduced in the membrane matrix by the chemical grafting of 4-vinylpyridine with the desired content. These membranes were extensively characterized for their surface morphology, thermal stability, water content, and surface-charge properties using SEM, TEM, FTIR, TGA, water uptake, and ion-exchange capacity measurements. Counterion transport numbers across these membranes were estimated from membrane potential data. Membrane conductance measurements were also performed and these data were used for the estimation of values of counterion diffusion coefficients in the membrane phase. Physicochemical and electrochemical properties of these membranes and equivalent pore radius (estimated from electroosmotic flux measurements) were found to be highly dependent on the 4-vinylpyridine (4-VP) content in the membrane phase. It was also observed that for better selectivity and membrane conductivity of anion-exchange membranes complete optimization of the loading of 4-VP in the membrane phase is necessary. Furthermore, among these, membrane with 25% loading with 4-VP exhibited very good selectivity, water content, and ion-exchange capacity along with moderate membrane conductivity, which may be used for their application in electro-driven separation at elevated temperatures or for other electrochemical processes.

Keywords: Composite membranes; Organic–inorganic composite; Anion-exchange membrane; Membrane conductance; Electroosmosis

1. Introduction

Ion-exchange membrane is now widely used in various applied electrochemical devices such as membrane electrolysis, solid polymer electrolyte, and fuel cell storage batteries as well as in the field of separation science, which includes electrodialysis, electro-deionization, etc. [1–4]. For the purpose of these processes under drastic conditions such as high temperatures and strong oxidizing conditions, a more stable ion-exchange membrane should be developed. Perfluorocarbon ion-exchange membranes were successfully applied for different industrial applications, but its high cost is a serious limitation [5]. Several types of polymers that are being used as homogeneous anion-exchange membranes after chloromethylation and amination with triamine or heterogeneous anion-exchange membrane have been reported [1,6–8]. These include: (i) copolymers of styrene and divinylbenzene [1], (ii) polysulfone [9,10], (iii) styrene and butadiene block copolymers [11], (iv) interpolymers of polyethylene and styrene-divinylbenzene copolymers [12,13], and (v) polyvinyl chloride-glycidyl methacrylate-divinylbenzene-based polymers [14]. During the preparation of these membranes, chloromethyl ether and solvents were used which are hazardous and not ecofriendly in nature. Thus it is desirable to develop an ecofriendly method for the preparation of thermally and dimensionally stable anion-exchange membranes in aqueous medium.

Organic–inorganic composites offer the possibility for new generation of nanostructured materials with diversified applications such as catalysts [15], electronic or pho-

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[*] Corresponding author. Fax: +91-278-2567562/2566970.
E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).

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tonic devices [16], and sensors [17]. Furthermore, the incorporation of inorganic materials on a nanoscale can enhance the retardancy and mechanical strength of organic polymers [18]. Reports are available, which provide a window for the preparation of organic–inorganic composites using 4-vinylpyridine. Organic–inorganic nanocomposites were used as enzyme bioelectrocatalysts [19]. The synthesis of vinyl polymer–silica nanocomposite material has been also reported in which 4-vinylpyridine was used for the introduction of positively charged functional groups [19]. Preparations of proton-exchange or cation-exchange membranes based on organic–inorganic composite polymers have also been reported [20–22]. But little work has been done on the preparation and application of organic–inorganic composite material in aqueous medium as anion-exchange membrane.

It was, therefore, the objective of this work to develop a new type of organic–inorganic composite, viz., thermally stable anion-exchange membranes in aqueous medium by an ecofriendly route. Polyvinyl alcohol–silica composite membranes were prepared and anion-exchange groups were introduced by the chemical grafting of 4-VP in varied compositions. These membranes were characterized by physicochemical and electrochemical studies and their properties were found to be dependent on the content of 4-VP in the membrane matrix.

2. Experimental

2.1. Materials and membranes preparation

Polyvinyl alcohol (PVA; MW: 125,000), hydrochloric acid, sodium hydroxide, sodium chloride, ammonium persulfate, and dimethyl sulfate of AR grade were obtained from S. d-fine Chemicals, India. Tetraethylorthosilicate (TEOS), 4-vinylpyridine (4-VP), and divinylbenzene were received from the Aldrich Chemicals and used as obtained. Double-distilled water was used in all experiments.

Five grams of PVA was dissolved in 100 ml of hot deionized water under constant stirring to obtain a homogeneous solution. Then the required quantity of the 4-vinylpyridine (monomer), divinylbenzene (4% w/w), and ammonium persulfate (4% w/w) was added and at 70 °C the mixture was kept for 1 h to get the semi-interpenetrating polymer network. Further equivalent amount of the dimethyl sulfate with respect to 4-vinylpyridine was added to quaternize the pyridinium group. The mixture was stirred for 2 h at room temperature to obtain a clear homogeneous solution. Then 2 ml of TEOS was added at room temperature and the mixture was kept under stirred condition for 24 h to get a gel. The resulting gel was cast on a clean glass plate with the desired thickness and dried at room temperature to obtain a film. By varying the amount of the 4-vinylpyridine with respect to PVA, different membranes with 15, 25 28, 33, and 35% loading were prepared. Also, different membranes with DVB content ranging between 1 and 10% (w/w) were prepared for the optimization of its content in order to get flexible membranes with good electrochemical properties. Dried membranes were immersed in a solution containing formaldehyde (54.1 g), sodium sulfate (150.0 g), sulfuric acid (125.0 g), and water (470.0 g) for 2 h at 60 °C for effective cross-linking. These membranes were conditioned in a 0.10 M HCl solution and 0.10 M NaOH solutions alternately several times and then equilibrated with the experimental solution before being subjected to physicochemical and electrochemical studies. Different anion-exchange membranes were designated as AEM-X where X is the 4-vinylpyridine content (%) in the membrane phase.

2.2. FTIR studies and CHN analysis

The FTIR spectra of different cation-exchange membranes were obtained using spectrum GX series 49387. CHN analysis was carried out with Perkin-Elmer-2400, CHNS/O analyzer.

2.3. Thermal and mechanical strength analysis

The degradation process and the thermal stability of the membranes were investigated using thermogravimetric analysis (TGA) (Mettler Toledo TGA/SDTA851 with Star software), under a nitrogen atmosphere using a heating rate of $10\,^{\circ}\mathrm{C}/\mathrm{min}$ from 50 to 800 °C. Differential mechanical analysis (DMA) for the mechanical strength of the membranes was carried out using Mettler Toledo DMA 861 with Star software in isothermal condition.

2.4. TEM and SEM studies

Surface morphology of the thoroughly dried membrane film was studied by transmission electron microscopy (TEM) (Jeol-1200 EX transmission electron microscope) with a tungsten electron source operating at an accelerating voltage of up to 120 kV. For scanning electron microscopy (SEM), gold sputter coatings were carried out on the desired membrane samples at pressures ranging between 1 and 0.1 Pa. Sample was loaded in the machine, which was operated at 10^{-2}–10^{-3} Pa with EHT 15.00 kV with 300 V collector bias using a Leo microscope. SEMs were recorded.

2.5. Water content and ion-exchange capacity (IEC) measurements

For the measurement of water content, the membrane samples (3 × 3 cm) were immersed in distilled water for 24 h, their surface was wiped with filter paper, and then wet membrane was weighed. Thickness of wet membrane was determined by means of a digital micrometer and membrane density for wet membrane was determined by dividing the wet membrane weight and volume. Following this, wet membrane was dried at a fixed temperature of 60 °C to