Journal of Membrane Science 372 (2011) 249–257

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Functionalized biopolymer based bipolar membrane with poly ethylene glycol interfacial layer for improved water splitting

A. Michael Rajesh, Mahendra Kumar, Vinod K. Shahi*

Electro-Membrane Processes Division, Central Salt & Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar 364002, India

ARTICLE INFO

Article history:
Received 23 October 2010
Received in revised form 5 February 2011
Accepted 9 February 2011
Available online 17 February 2011

Keywords:
Modified chitosan
Poly ethylene glycol
Bipolar membrane
Electrodialysis
Water dissociation

ABSTRACT

This study investigates the effect of poly ethylene glycol (PEG) of different molecular weight (MW) as interfacial layer (IL) of bipolar membrane (BPM) for water dissociation. Chitosan (CS) was modified to *N*-methylene phosphonic chitosan (PC) and quaternized chitosan (QC), for preparing cation- and anion-exchange layer (CEL and AEL, respectively) of BPM. Different BPMs were prepared by layer-by-layer solution casting method (in aqueous media to achieve the good adhesion between layers) using PEG of different MWs (200–3400 Da) as IL. CEL and AEL with good ion-exchange properties were separately evaluated for their physicochemical and electrochemical characterizations. All BPMs with IL (PEG) were evaluated from current–voltage (*I–V*) curves and water dissociation efficiency. The experimental results proved the excellent catalytic activity of PEG for water dissociation, which further improved with its MW. Furthermore, electrodialysis with bipolar membrane (EDBPM) experiments confirmed the occurrence of water dissociation at BPM interface and thus formation of acid and base.

1. Introduction

BPMs composed of CEL, AEL and an IL between two layers [1–5]. Under the influence of an electric field, water split into H^+ and OH^- at BPM interface and the resultant ions (H^+ and OH^-) migrated towards cathode and anode compartments, respectively [6]. BPMs have been used for the production of acids and bases from salt solutions on industrial scale, pollution control, chemical processing with high efficiency, and low waste disposal [7,8]. Generally, thin IL (water dissociation catalyst) is introduced between CELs and AELs to improve the BPM performance. The catalytic mechanism for water dissociation at IL is considered as proton transfer reaction and depends on applied voltage. The functional groups present in the membrane matrix show the great significance for water dissociation [9,10].

An efficient BPM should have high selectivity, water dissociation efficiency, low salt diffusion, acid and base stability over wide pH range, along with good thermal and mechanical stability. These desired properties can be obtained by suitable membrane forming material, selection of IL and membrane casting methodology. Water dissociation occurs at the bipolar junction (IL) between ion-exchange layers (CEL and AEL) of BPM and significantly depends on their properties [1,3,11,12].

Strathmann et al. proposed multilayers BPMs with very thin IL of insoluble polyelectrolyte complex (poly(4-vinylpyridine) and poly(acrylic acid)) and demonstrated the enhanced catalytic water dissociation [13]. In another approach, water dissociation voltage was reduced by introducing metallic salt ($CrCl_3$) as IL catalyst [14]. The heavy metal ion complexes of ruthenium trichloride, chromic nitrate, indium sulfate, and hydrated zirconium oxide were used as IL to enhance the water dissociation efficiency of BPMs [14–17]. Hydrophilic polymer (poly HEMA/MPD cross-linked with TMC) was also used as IL to adhere the commercial ion-exchange membranes (NEOSEPTA® CM-1 and AM-1; Tokuyama Co. Ltd., Japan) for developing BPMs [18]. Xu and co-workers reported the starburst dendrimer (polyamidoamine (PAMAM)) [19], PEG [20], and poly vinyl alcohol (PVA) [21] as water dissociation catalysts at IL. PEG is a water soluble hydrophilic polymer with variable MW and size, which can be used as spacer to adhere CEL and AEL. There are possibilities of hydrogen bonding and polar interactions between PEG and water molecules, which also may accelerate the water dissociation efficiency of BPMs [22]. Recently, Balster et al. used different polyelectrolytes as IL and prepared tailor made BPMs. BPMs with pyridine based IL was efficient for water dissociation catalytic activity [23].

Thus, systematic study on effect of PEG molecular weight or size as IL on water dissociation efficiency is necessary to develop the highly efficient BPMs. The modified CS (PC and QC) was selected for fabrication of CEL and AEL due to easy functionalization of CS (hydrophilic biopolymer), good chemical and thermal stabilities,

* Corresponding author. Tel.: +91 278 56 94 45; fax: +91 278 56 69 70.
E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).

0376-7388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2011.02.009

Nomenclature

List of symbols

T	absolute temperature (K)
I	applied current density (mA cm^{-2})
V	applied potential (V)
ρ	cross-linking density
I	current (A)
η	current efficiency
χ_c	degree of crystallinity
χ^m	surface charge concentration
D^m	diffusion coefficient of ion through membrane
V_{diss}	dissociation potential (V)
R_{diss}	dissociation resistance (Ω cm^2)
ΔH_m	enthalpy of melting (J g^{-1})
A	effective membrane area (m^2)
W	energy consumption (kWh mol^{-1})
ϕ	front factor
i_{lim1}	first limiting current density (mA cm^{-2})
F	Faraday's constant (96,500 C mol^{-1})
R	gas constant (8.314 J mol^{-1} K^{-1})
$dc_{OH-\text{ or }H+}/dt$	the change in acid (H^+) or base (OH^-) concentration in AC or BC, respectively (mol m^{-3})
E'	modulus (Pa)
A	membrane area (m^2)
d	membrane density
Δx	membrane thickness (cm)
κ^m	membrane conductivity (S cm^{-1})
P_s	membrane permselectivity
V_{op}	operating potential (V)
R_{op}	operating resistance (Ω cm^2)
i_{op}	operating current density (mA cm^{-2})
J	water dissociation flux (mol m^{-2} s^{-1})
i_{lim2}	second limiting current (mA cm^{-2})
n	stoichiometric number (n = 1 in this case)
Δt	time allowed for electro-membrane process (s)
V	total volume (cm^3)
m	weight (g)
φ_w	water uptake

non-toxicity and biodegradability [24–31]. Furthermore, the presence of –OH and –NH_2 groups onto the CS matrix, afford the grafting and cross-linking to achieve the high surface charge concentration and membrane stabilities [30]. Also layer-by-layer solution casting of CEL, IL and AEL in same solvent (water) seems to be most attractive because of its simplicity, cost effectiveness and eco-friendly in nature. The main objective of the present study is to prepare inexpensive BPMs using modified CS (PC and QC) with PEG as IL and further their characterizations. Presence of PEG at IL accelerated the water dissociation efficiency and reduced the voltage across the membrane. The effect of MW of PEG as IL on water dissociation efficiency was fully investigated and found that water dissociation efficiency of BPM increased with MW of PEG.

2. Experimental

2.1. Materials

Chitosan (100% deacetylation), poly(vinyl alcohol) (PVA; Mw: 125,000 Da), phosphorous acid (99% purity) and poly ethylene glycol (PEG) of 200, 2000, and 3400 Da molecular weights, were received from Sigma–Aldrich chemicals and used without further purification. CH_3I, NaCl, HCHO, glacial CH_3COOH, CH_3OH, H_2SO_4, HCl, and NaOH (AR grade, S.D. Fine Chemicals, India) were used as received. Double-distilled water was used in all experiments.

2.2. Functionalization of chitosan and membrane preparation

PC was synthesized from 2% (w/v) CS solution in glacial acetic acid 1% (v/v). One part (by weight) of CS was used and 1 part of phosphorous acid (by weight) dissolved in water, was added drop-wise with continuous stirring for 1 h. Then, the temperature of the reaction vessel was raised up to 70 °C and 1 part of 36.5% formaldehyde (by weight) was added drop-wise in 1 h and further heating was maintained for 6 h. The viscous solution was obtained after the removal of ~75% (v/v) solvent by evaporation under vacuum that was precipitated in acetone and dried under vacuum at 50 °C for 24 h. Also, QC was synthesized by dissolving 2.5% (w/v) CS in 42% methanol and the resultant mixture was kept at 30 °C under constant stirring for 1 h. Then, 5% NaCl solution (w/v) and 5% (v/v) CH_3I was added at 4 h intervals in 2:1:1 proportion under constant stirring. The reaction mixture was refluxed at 70 °C for 12 h and the viscous solution was obtained after the removal of ~75% (v/v) solvent by evaporation under vacuum that was precipitated in acetone and dried under vacuum at 50 °C.

The separate solutions were prepared by dissolving the functionalized CS (PC and QC) and PVA (80%, w/w) in distilled water with constant stirring at 30 °C to prepare CEL and AEL. Air bubbles were removed by applying vacuum to obtain a clear solution that was casted on a clean glass plate covered with a high density poly (ethylene) sheet. Thin films of desired thickness were dried at 60 °C for 24 h in vacuum. Thus obtained water soluble transparent thin films were cross-linked by formal reaction using the cross-linking solution having formaldehyde (HCHO) (54.1 g), sodium sulfate (150 g), sulfuric acid (125 g), and water (470 g) for 2 h at 60 °C. Resultant membranes were equilibrated in 0.10 M HCl and NaOH solutions alternately several times and stored in distilled water for further physiochemical and electrochemical studies.

For the preparation of BPM, CEL was prepared and dried under IR lamps. Thin layer (10 μm) of PVA–PEG (25%, w/w) gel was casted onto top surface of CEL followed by drying under IR lamps for complete solidification of the layer. On the top of this layer, AEL of desired thickness (150 μm) was casted and the resultant composite membrane was allowed to dry under IR lamps and further at 60 °C in a vacuum oven. The layer-by-layer solution casting method was used to achieve the good adhesion between (CEL, IL and AEL) [32]. Firmed contacts between CEL, AEL and IL were possible because all polymer solutions were prepared in the same solvent (distilled water) [33]. The obtained BPM films were then immersed in a cross-linking solution and heated at 60 °C for 2 h to achieve the effective cross-linking by formal reaction. Resultant membranes were conditions in 0.10 M HCl and NaOH solutions alternately several times and stored in distilled water for further physiochemical and electrochemical studies. The membranes thus prepared were designated as PC – QC/X, where X is the molecular weight of PEG.

2.3. Instrumental analysis

FTIR spectra of dried uncross-linked, cross-linked AEL and CEL were recorded by ATR technique with spectrum GX series 49387 spectrometer in the range of 4000–600 cm^{-1}. Scanning electron microscopy (SEM) images of the dried CEL, AEL and cross-sectional image of BPMs were recorded by using a LEO Instruments (Kowloon, Hong Kong) microscope after the gold sputter coatings on a desired layers and membrane samples. Differential scanning