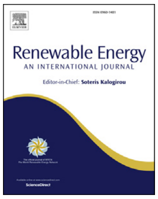
Renewable Energy 86 (2016) 922–929

Contents lists available at ScienceDirect

Renewable Energy

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



Synthesis and properties of novel proton exchange membranes based on sulfonated polyethersulfone and N-phthaloyl chitosan blends for DMFC applications

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A R T I C L E   I N F O

Article history:
Received 1 February 2015
Received in revised form
27 July 2015
Accepted 7 September 2015
Available online xxx

Keywords:
N-phthaloyl chitosan
Sulfonated polyethersulfone
Proton exchange membrane
Direct methanol fuel cell
Methanol permeability

A B S T R A C T

Chitosan is modified by phthaloylation using an excess of phthalic anhydride at 130 °C and blended with the sulfonated polyethersulfone (SPES) to produce composite blend membranes. In particular the introduction of the phthaloyl group into the chitosan matrix increases its solubility in organic solvent, film formability, flexibility, low methanol permeability and with suitable ion conductivity. SPES and N-phthaloyl chitosan (NPHCs) blend membranes with various compositions were prepared and detailed investigation on water uptake, proton conductivity and methanol permeability has been conducted for its suitability in fuel cell environments. Methanol permeability studies envisaged that NPHCs blend membranes are impervious to methanol. The thermograms display the good thermal stabilities of blend membranes than Nafion-117. Relatively high selectivity parameter values of these membranes indicated their greater advantages over Nafion-117 membrane for targeting on fuel cell applications, especially in direct methanol fuel cell (DMFC) environments.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) have been paying immense interest as new energy conversion technologies for their promising applications in clean power source. One of the key components of the PEMFC is the proton exchange membrane (PEM) which acts as both electrolyte and as a separator between the anode and cathode components. Nafion, a perfluorinated PEM, has been used in the fuel cell technologies due to their high proton conductivity and substantial stabilities [1–5]. Although these membranes showed very high conductivity, their three major drawbacks: very high cost; loss of proton conductivity at very high temperature; and high methanol permeability, drastically reduces their DMFC performance [6–9]. The disadvantages of these materials and the demand for new and clean energy conversion/production systems have initiated world-wide research activities on the development of alternative membrane materials for polymer electrolyte membrane fuel cells.

Among the various materials suggested, poly arylene ethers are seen as the most promising one due to their outstanding chemical and thermal stabilities and high glass transition temperature (T_g) and oxidative resistance [10,11]. Sulfonation of polyethersulfone (PES), another member in the family of poly (arylene ether sulfone), has created more interest in ion exchange membranes. However, these membranes have also some limitations such as moderate proton conductivity and it is necessary to enhance it by blending with other polymeric materials.

In recent years, synthetic and natural polymer composite membranes have made a significant impact as polymer electrolytes in the fuel cell environment. Among the natural polymers, chitosan, a polysaccharide bio resource, biodegradable and its biocompatible properties that have been made this polymer as promising and low cost source of membrane material. It has been extensively investigated as a solid polymer electrolyte in low and intermediate temperature polymer electrolyte – based fuel cells [12]. Solid polymer electrolytes are generally classified into two classes: ion-solvating polymer composites and polyelectrolyte. Chitosan can serve as both polyelectrolyte membranes, and as a matrix material for ion-solvating polymer composite membranes.

Utilization of a chitosan biopolymer for fuel cell technologies is novel and challenging where biological products are usually considered as waste, non-hazardous and environmentally benign [13,14]. However, utilization of chitosan has been delayed, probably

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http://dx.doi.org/10.1016/j.renene.2015.09.018
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because of the difficulty to dissolve in general organic solvents. This is due to their rigid crystalline structure caused by the establishment of hydrogen bonding between their amino and hydroxyl groups within a chitosan monomer and monomers. In decree to master this problem, the structure of chitosan has been modified using hydroxyalkylation, carboxyalkylation, and acylation processes, to mention a few [15]. A highly reactive primary amino group of chitosan is convenient for chemical modification, having better solubility in organic solvent, makes it easier to compose with other polymer to get a homogenous blend [16,17]. N- phthaloylation of chitosan with phthalic anhydride is an efficient way to improve its organic solubility [15]. The structural modification was utilized to modify the Chitosan properties for preparing composite membranes with better hydrophilicity and surface charge [18].

SPES is a useful material in membrane technology, which could ensure conducting properties and structural stability and NPHCs could provide the requisite water retention properties of the composite blend [19]. This paper describes an approach for the fabrication of SPES and NPHCs composite ion exchange membranes in different compositions and they were characterized for its adaptability in the fuel cell environment.

2. Methodology

2.1. Materials

PES (Gafone 3200P, M_w 123 kDa) was provided by Ghardha chemicals Ltd., India, Creamish white chitosan flakes (75–85% degree of deacetylation) was supplied by Pelican Biotech and Chemical Labs Pvt. Ltd., Kerala, India as a gift sample. Concentrated sulfuric acid (98%) (Merck, India) and chlorosulfonic acid (Loba Chemie, India) were used as received. N-methyl-2-pyrrolidone (NMP) (Merck, India) has been used as a solvent for the preparation of membrane and sodium chloride received from Loba Chemie, India for determining ion exchange capacity.

2.2. Preparation of SPES

PES was dried for more than 12 h in an oven at 80 °C; 10 g of polymer dissolved in 100 ml of concentrated sulfuric acid at room temperature to achieve complete dissolution of the polymer in the solvent. Then adequate amount of chlorosulfonic acid was added to the reaction mixture under continuous stirring. The sulfonation reaction was carried out at 45 °C to ensure proper sulfonation. Then the polymer solution was gradually precipitated into a large excess of ice-bath water and washed with distilled water until the pH is 7. The polymer was then dried in an oven at 80 °C for 24 h. The degree of sulfonation (DS) was determined by titration method and it was found to be 35%. The sulfonated polymers with a degree of sulfonation of 40% endured in cold water, but were found to start dissolving in boiling water. The high DS provides high ionic conductivity and high hydrophilicity but less stable and soluble in hot water. Therefore the membrane samples with an optimum degree of sulfonation were chosen for further studies.

2.3. Preparation of NPHCs

Chitosan modification was done according to the procedure reported by ohya et al. [20]. Initially 23.7 g of chitosan were reacted with 64.5 g of phthalic anhydride in 100 ml N, N-dimethyl formamide (DMF) at 130 °C for about 5 h, under nitrogen atmosphere. The reaction mixture was poured into a large amount of ice cold water to precipitate NPHCs. It was then, filtered and purified by ethanol and ethyl ether to obtain yellow solid with 80.6% yield. Synthetic route for the preparation of NPHCs is shown in Fig. 1.

2.4. Preparation of composite membranes

SPES/NPHCs composite blend membranes were prepared by solvent evaporation technique. Composition of the casting dope together with the code of the membrane prepared is given in Table 1. Several ratios of SPES/NPHCs were dissolved in NMP individually at 60 °C for 8 h on a hot plate and stirred until a viscous and clear solution was obtained. The solution was strained by a sand filter immediately. Then the polymeric solution was cast on a glass plate using a doctor blade and the thickness of the as-cast film was adjusted between 0.20 mm and 0.25 mm. After casting, the film was dried in an oven at 110 °C for 24 h and 80 °C in vacuum oven for 12 h to remove the traces of solvent. After cooling to room temperature, the membrane was peeled off from the glass plate by immersing it in deionized water.

2.5. Characterization methods

2.5.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were used to confirm the pendant $-SO_3H$ group on the polymer chain as well as the possible interactions between SPES and NPHCs in the composite blend membranes. The FTIR spectrometer (BRUKER) was used for analysis and the spectra were measured over a wave number range of 4000–500 cm^{-1} in absorbance mode.

2.5.2. X-ray diffractometer

The crystalline structure of samples was characterized by the X-ray diffractometer (Panalytical, Xpert-Pro) using copper Kα ($\lambda = 1.54056 \times 10^{10}$ m) radiation.

2.5.3. Ion exchange capacity

The ion exchange capacity (IEC) was assessed by the titration method. The dried membrane in the protonic form was immersed in 1 M NaCl solution for 24 h at room temperature. The H^+ ions, substituted by Na^+ ions, were released into the solution. The solution was then titrated by a 0.012 M NaOH solution using phenolphthalein as an indicator. The IEC of the membranes were calculated using the following equation

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{W_{Dry}} \tag{1}$$

where C_{NaOH} (mol/L) and V_{NaOH} (ml) are the concentration and volume of NaOH solution required for neutralization of the residual solution, and W_{Dry} is the weight of the dry sulfonated membrane.

2.5.4. Water uptake

Water uptake of blend composite membranes was determined by measuring the variation in weight before and after the hydration. The membranes were immersed in deionized water at room temperature for 48 h. The membranes were then taken out, wiped off the surface water with blotting paper and wet weight was weighed. Then the membranes were dried under vacuum at 100 °C overnight and weighed. The weight difference before and after the hydration relative to the dry membrane weight was calculated as water uptake percentage.

$$\text{Water Uptake } (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{2}$$

2.5.5. Thermogravimetric analysis

The thermal stability of the composite blend membranes was examined by the thermogravimetric analyzer (SDTQ600, TA