Sorption and transport properties of 2-acrylamido-2-methyl-1-propanesulfonic acid-grafted bacterial cellulose membranes for fuel cell application

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HIGHLIGHTS

► This work pioneers the exploration of bacterial cellulose-based proton-conducting membranes for DMFCs.
► An effective modification of BC membrane with high conductivity is proposed.
► The modified BC membrane exhibits exceptional methanol-inhibiting behavior.
► The AMPS10-*g*-BC membrane used in DMFC is advantageous to be operated under higher methanol concentration.

ARTICLE INFO

ABSTRACT

This study investigated the sorption and transport properties of proton-conducting membranes based on a bacterial cellulose (BC) biopolymer with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) grafted using ultraviolet (UV)-induced polymerization. The transport properties of the membranes were characterized according to their self-diffusion coefficients and methanol permeabilities. Using pulsed field-gradient nuclear magnetic resonance (PFG-NMR) technology, the water and methanol self-diffusion coefficients through the AMPS-*g*-BC membrane were identified as 1.48×10^{-5} cm^2 s^{-1} and 5.30×10^{-6} cm^2 s^{-1}, respectively. The methanol permeability of the AMPS-*g*-BC membrane was 5.64×10^{-7} cm^2 s^{-1}, which was approximately 42% of that of Nafion 115. The differences in the transport behaviors of the Nafion 115 and AMPS-*g*-BC membranes correlated with the sorption characteristics of solvent uptake and lambda (λ) values (number of solvent molecules absorbed per sulfonic acid). The ratio of the water and methanol λ values (i.e., $\lambda_{CH_3OH}/\lambda_{H_2O}$) for the AMPS-*g*-BC membrane was 0.07, which indicated its sorption preference for water compared to methanol. Overall, results indicate that the AMPS-*g*-BC membrane is an effective methanol barrier and a potential solid electrolyte candidate for direct methanol fuel cells.

1. Introduction

Proton-conducting membranes play an important role in fuel cell technology because of their use as separators and proton conductors. Nafion, the current commercially used perfluorosulfonic acid membrane, has a cluster structure with phase separation performed by its hydrophobic fluorocarbon and pendant sulfonic acid groups [1]. Although the Nafion membrane shows good stability and high proton conductivity, some serious drawbacks exclude it from application in direct methanol fuel cells (DMFC). Its major drawback is its unacceptably high methanol permeability, which leads to fuel waste and loss of performance at the cathode because of oxygen consumption and catalyst poisoning [2,3]. Therefore, proton exchange membrane (PEM) materials with low methanol permeability and high proton conductivity are particularly desirable for early commercialization of DMFC.

Recent studies have investigated alternative economic materials with novel hydrocarbon polymers synthesized or combined with a methanol-inhibiting material [4–6]. Investigators have proposed sulfonated aromatic hydrocarbon polymer membranes as low cost alternatives to Nafion. The additional advantages of sulfonated aromatic hydrocarbon membranes are thermal stability and low methanol permeability. However, their proton conductivities are inferior to that of Nafion [7]. Poly(2-acrylamido-2-methyl-1-

propanesulfonic acid) (PAMPS) displays higher proton conductivity than partially hydrated Nafion because of the sulfonic acid groups in its chemical structure; thus, it forms a component in a novel proton-conducting electrolyte membrane [8,9]. However, because PAMPS is highly water-soluble, a major research objective has been to fix the PAMPS in stable structures while maintaining its high proton conductivity; for example, through the introduction of a copolymer [9,10].

Bacteria produce bacterial cellulose (BC) [11] through the linkage of β-1.4 glycoside to β-D-glucose. Approximately 10 of the linked chains form a microfibril, and then several to >100 of the microfibrils form a fibril. The diameter of BC microfibrils is approximately 20–50 nm. The microfibrils form a three-dimensional reticulum matrix through hydrogen bonding. BC has unique physical properties, including high mechanical stiffness and strength, high moisturizing nature, high crystallinity, broad chemical modifying capacity, and biodegradability [12]. Previous studies have used chemical treatments to improve the electro-mechanical properties of cellulose [13–15].

In principal, a logical method for the development of PEM materials would allow the passage of water but restrict the movement of methanol. The solubility and diffusion properties of the permeating solvent in the membrane, at the given temperature and conditions, determine membrane permeability. The solubility of the solvent in the polymeric membrane is dependent on the chemical nature of the solvent and the corresponding membrane, whereas diffusion is mainly determined by the morphology of the membrane and the properties of the solvent [16]. Sorption data provide a qualitative measure of the solubility of a solvent into a polymer; however, they do not provide information on the diffusion of the solvent into the polymer. Previous studies have described that the water/methanol uptake per Nafion sulfonic acid group is equal in membranes equilibrated in pure water and in pure methanol [17,18]. Huang et al. [18] and Hietala et al. [19] reported that the water and methanol self-diffusion coefficients in the Nafion membrane and in solution display nonsignificant differences.

Although several investigators [20–22] have proposed the potential use of BC as a material source for environmentally compatible ion-exchange membranes for fuel cells, a study on a BC-based proton-conducting membrane for DMFC has yet to be published. This study, therefore, investigated BC-based proton-conducting membranes by modifying bacterial cellulose membranes with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) using ultraviolet (UV)-induced grafting polymerization. It aimed to establish the relationship between the transport and sorption properties of water and methanol in the membranes and their DMFC power performances.

2. Experimental

2.1. Materials

2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was purchased from Merck, Germany. The BC membrane was supplied by the Food Industry Research and Development Institute (FIRDI), Taiwan. Benzophenone (BP), isopropanol, acetone, and methanol were purchased from Aldrich, USA.

2.2. Preparation of membranes

Scheme 1 displays the preparation procedures for grafting AMPS monomers onto the BC biopolymer using BP as a photoinitiator. During the radiation procedure, a BC membrane was immersed in BP methanol solution for 3 h. It was then activated using UV light (400 W, 110–400 nm mercury lamp) for 60 s in a nitrogen

atmosphere. As shown in Scheme 1(a), during this step, BP abstracted hydrogen atoms from the membrane substrate (BC) to generate surface radicals and semipinacol radicals, which combined to form surface photoinitiators [23]. An AMPS solution (10–20 wt.%) was then added to the reaction chamber and irradiated with UV light for 1 min. As shown in Scheme 1(b), during this step, the introduction of the monomer (AMPS) to the active membrane substrate (BC) initiated the graft polymerization process. The resulting AMPS-g-BC membrane was then washed several times with methanol/acetone to remove unreacted homopolymers and monomers.

2.3. Characterization of membranes

2.3.1. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was performed in a transmittance mode using a spectrophotometer (Spectrum One, Perkin Elmer, USA). Four scans were collected in all spectra at a resolution of 32 cm^{-1}.

2.3.2. Themogravimetric analysis (TGA)

Membrane TGA measurements were collected in a nitrogen atmosphere. The tested samples were 10 mg in weight and the heating rate was 10 °C min^{-1}. Thermograms were obtained in the temperature range 30–700 °C.

2.3.3. Degree of AMPS grafting

The degree of AMPS grafting was evaluated according to changes in membrane weight pre- and postgrafting polymerization using the following equation [24]:

$$DOG = \frac{m_{\text{grafted}} - m_{\text{initial}}}{m_{\text{initial}}} \times 100\% \tag{1}$$

where DOG is the degree of grafting (i.e., the ratio of the weight gain), m_{initial} is the initial BC membrane weight, and m_{grafted} is the membrane weight after the grafting process.

2.3.4. Water/methanol solvent uptake

The water/methanol solvent uptakes of the membranes were determined according to differences in the membrane weights pre- and postimmersion in the water/methanol solution overnight. The surface of the membrane sample was wiped with filter paper to remove excess water, after which the wet membrane (W_{wet}) was weighed immediately. The dry membrane (W_{dry}) was weighed after drying at 60 °C for 24 h. The water/methanol solvent uptake (%) was calculated using the following equation:

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

2.3.5. Ion-exchange capacity and lambda value

A titration method was used to determine the ion-exchange capacity. Each membrane sample was soaked in 50 ml of a 1 M sodium chloride aqueous solution overnight to exchange protons with sodium ions. The ion-exchanged solution was then titrated with a 0.005 M sodium hydroxide solution. The ion-exchange capacity was determined using the following equation:

$$IEC = \frac{M_{\text{i,NaOH}} - M_{\text{f,NaOH}}}{W_{\text{dry}}} = \frac{H^+ \, (\text{mmol})}{W_{\text{dry}}} \tag{3}$$

where $M_{\text{i, NaOH}}$ is the initial mmol of NaOH for titration and $M_{\text{f, NaOH}}$ is the mmol (m_{eq}) of NaOH postequilibrium, H^+ is the molar