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Bacterial nanocellulose/Nafion composite membranes for low temperature polymer electrolyte fuel cells

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HIGHLIGHTS

- A series of novel nanocomposite membranes of BC and Nafion are fabricated for DMFC.
- The novel BC/Nafion membranes were reinforced with concrete-like structure.
- Membranes show high strength, good proton conductivity and low methanol permeability.
- The annealed membranes are more suitable for DMFC.
- High PEMFC and DMFC performances are obtained from annealed B1N7 membranes.

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ABSTRACT

Novel nanocomposite membranes aimed for both proton-exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are presented in this work. The membranes are based on blending bacterial nanocellulose pulp and Nafion (abbreviated as B*x*N*y*, where *x* and *y* indicates the mass ratio of bacterial cellulose to Nafion). The structure and properties of B*x*N*y* membranes are characterized by FTIR, SEM, TG, DMA and EIS, along with water uptake, swelling behavior and methanol permeability tests. It is found that the B*x*N*y* composite membranes with reinforced concrete-like structure show excellent mechanical and thermal stability regardless of annealing. The water uptake plus area and volume swelling ratios are all decreased compared to Nafion membranes. The proton conductivities of pristine and annealed B1N9 are 0.071 and 0.056 S cm^{-1}, respectively, at 30 °C and 100% humidity. Specifically, annealed B1N1 exhibited the lowest methanol permeability of 7.21×10^{-7} cm^2 s^{-1}. Through the selectivity analysis, pristine and annealed B1N7 are selected to assemble the MEAs. The performances of annealed B1N7 in PEMFC and DMFC show the maximum power densities of 106 and 3.2 mW cm^{-2}, respectively, which are much higher than those of pristine B1N7 at 25 °C. The performances of the pristine and annealed B1N7 reach a level as high as 21.1 and 20.4 mW cm^{-2} at 80 °C in DMFC, respectively.

1. Introduction

Proton conducting membrane is one of the essential and critical materials in both proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC). Compared to PEMFC, DMFC is considerably more suitable for powering portable electric devices, such as laptops and cameras, because of its high power density [1,2]. However, the methanol crossover caused by the intrinsic property of commercial membranes, i.e. Nafion, results in about

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40% loss of fuel when 2 M methanol aqueous solution is fed. The migrated methanol poisons the cathode catalyst by being oxidized inducing an overpotential at the electrode [2,3]. Moreover, in the presence of ruthenium (Ru) in the anode catalyst, which is advantageous to reduce carbon monoxide (CO) poisoning, Ru can be carried by methanol crossover and thus the DMFC performance significantly diminishes [2]. Additionally, high cost of Nafion, \$600–1200 m^{-2}, is another barrier for its extended applications [2]. Therefore, novel proton exchange membranes (PEMs) with high ion conductivity and low methanol permeability are vitally required to be developed.

To date, different methodologies and strategies have been applied to fabricate PEMs for DMFC, either via grafting [4], cross-linking [5], or combining polymer electrolytes with nanoparticles [6], carbon nanotube [7], graphene oxide [8], and acid–base complex [9], or by employing layer-by-layer (LBL) [10], and blending [11] methods. Among them, blending is an easy and efficient technique to improve PEMs properties. One strategy is to blend Nafion with methanol blocking materials such as PVA [12,13], PTFE [14], PVDF [15] and SiO_2 [6], and the other one is to blend proton donors with hydrocarbon polymers including PVA [5,16,17], PBI [18] and SPEEK [19].

Bacterial cellulose (BC), mainly generated by the genus *Gluconacetobacter*, (formerly *Acetobacter* sp.), in particular *G. xylinus* and *G. hansenii*. Furthermore, it could be produced from a traditional beverage culture called Kombucha that is a symbiont of *Gluconacetobacter* and one or more yeasts [20]. Essentially, BC is a kind of pure cellulose material with special 3D nanostructure morphology formed by nanofibrils with the diameter of 20–100 nm [21–23]. Its distinguished properties from plant cellulose include high crystallinity, high tensile strength, high water binding capacity, low gas permeation and good biocompatibility [23]. BC has been reported to be used as a pervaporation membrane to separate ethanol and water [24,25], which implies that BC membrane is capable to have a low alcohol permeability. In addition, a sulfonated regenerated cellulose membrane and a cellulose acetate membrane that have a similar structure as BC, have been reported to work as a potential membrane and a separator in DMFC respectively [26,27]. Combining those two examples, it is reasonable to deduce the possible application of BC in DMFC. Most recently, 2-acrylamido-2-methyl-1- propanesulfonic acid-grafted BC membranes was synthesized and reported its application in DMFC, which partially testified the deduction above [29]. To prove the potential application of BC in DMFC, an easy and direct fabrication methodology needs to be developed.

In this work, a series of BC/Nafion nanocomposite membranes have been prepared by incorporating BC pulp into Nafion solution, and their potentials both in PEMFC and DMFC were evaluated. Since the annealing process has significant effects on Nafion contained membranes [29], the differences between pristine and annealed BC/Nafion membranes were studied and characterized thoroughly by FTIR, TGA, DMA, SEM, water uptake capability, swelling property, proton conductivity, methanol permeability and selectivity, as well as single cell tests in PEMFC and DMFC systems.

2. Experimental

2.1. Fermentation and purification of bacterial cellulose

Kombucha was purchased from local market and used to produce large amounts of bacterial cellulose pellicles in this study. The fermentation medium was the same as the seed medium and the preparation was as follows. Cool tea infusion was made by soaking 0.5% (w/v) green tea in boiling deionized (DI) water for 20 min and then was used to dissolve 5% (w/v) D-glucose, 0.5% (w/v) yeast extract (Oxoid, UK), and 0.3% (w/v) tryptone (Oxoid, UK). Then the brownish liquid culture medium was split into pre-autoclaved flasks with lids followed by pasteurization without pH regulation.

A Kombucha pellicle preserved in a seed medium was chosen as the seed inoculum. The pellicle was cut into small pieces with a sterilized scissor in a sterile hood and one or two pieces were inoculated into a 100 mL fermentation medium. After static incubation at 30 °C for seven to ten days, thick yellowish BC pellicles formed at the top of the cultures.

BC pellicles were harvested and rinsed with the DI water to remove soluble medium components and then treated in 1.0% sodium hydroxide solution for 2 h at 80 °C to eliminate attached bacterial cells and other impurities. Thereafter, BC pellicles were further purified by boiling in the DI water for 2 h. The purification process was repeated until the BC samples changed to milky color or semitransparent. Finally, the BC hydrogels were rinsed with the DI water until the pH value of the eluent was neutral and the absorbance at 280 nm of the eluent was the same as water. The purified BC pellicles were stored in the DI water at 4 °C for further use.

2.2. Preparation of bacterial cellulose pulp

Similar to the method used by Helbert et al. [30], a food blender was applied to homogenize BC. Small pieces of BC pellicles and DI water of threefold weight of the BC gel were placed into the food blender, and then the BC pulp was prepared by continuously cutting at a full speed for 30 min until no big gel piece was observed. The homogenous BC pulp was poured into a sterilized container with a lid, sealed with parafilm and preserved at 4 °C. Triplicate pulp samples of 10 mL were dried at 105 °C overnight and weighed to determine the content of dry mass in the BC pulp. An appropriate BC concentration range was 3–5 mg L^{-1}.

2.3. Preparation of BC/Nafion blending membranes

Considering the insolubility of Nafion in water, different amounts of 5% Nafion solution (Dupont) were added in the mixture of BC pulp, n-propanol and ethanol (45:48:2, w/w) and stirred at low speed under room temperature overnight. The homogenous suspension was concentrated by vacuum distillation in a rotary evaporator at 50 °C followed by cooling and degasing in a vacuum drying oven for 15 min. Then, the condensed pulp was transferred into glass Petri dishes and de-bubbled with capillary tubes in order to cast into the BC/Nafion blend membranes under room temperature.

Few days later, the formed BC/Nafion membranes were peeled off from the petri dishes carefully after immersing in DI water overnight. In order to eliminate soluble impurities, the harvested BC/Nafion membranes were rinsed with DI water until no alcohol could be detected in the immersion liquid by comparing O.D. value of rinsing water with that of the blank control group at 525 nm after they were reacted with acidic potassium permanganate. Thereafter, the BC/Nafion membranes were dried at ambient temperature and half of them were annealed at 110 °C for 1 h just like the PVA/Nafion blends [29].

2.4. Characterization of BC/Nafion membranes

The BC/Nafion membranes were characterized by attenuated total reflection fourier transform infrared (ATR-FTIR) spectra. The membrane samples were placed on an infrared spectrometer (NEXUS-670, Nicolet-Thermo) covering the diamond of ATR instrument, then spectrograms with a wavenumber resolution of 4 cm^{-1} in the range from 4000 to 650 cm^{-1} were obtained.