



Novel pore-filled polyelectrolyte composite membranes for cathodic microbial fuel cell application



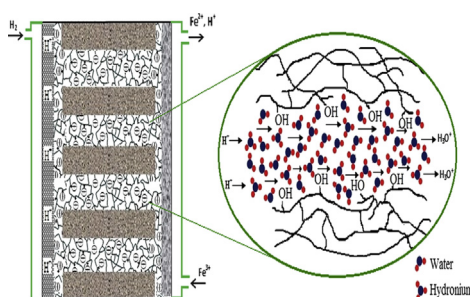
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HIGHLIGHTS

- Novel PVA pore-filled polycarbonate proton exchange membrane.
- Investigation of membrane physicochemical properties with PVA cross-link time.
- Pore-filled membranes showed very good performance and stability.
- Microbial fuel cell eliminates Pt catalyst at cathode and Nafion membrane use.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 March 2013
 Received in revised form
 11 May 2013
 Accepted 1 June 2013
 Available online 11 June 2013

Keywords:

Pore-filled membrane
 Poly(vinyl alcohol)
 Microbial fuel cell
 Cross-linking
 Biogenerator

ABSTRACT

Novel pore-filled polyelectrolyte membrane (PEM) was produced using track etched polycarbonate (PC) as porous substrate and poly(vinyl alcohol) (PVA) as pore filling material. PVA in PC pores was stabilized through cross-linking of PVA matrix with glutaraldehyde (GA). Cross-link time was varied from 24 h to 96 h while keeping the membranes in GA solution. Pore sizes of substrate PC membrane tested were 0.01, 0.1 and 0.2 μm . The membranes were characterized by Fourier-transform infrared spectroscopy and scanning electron microscopy. Ionic conductivity, water uptake, contact angle and gel content have been measured to determine membranes performance. The ionic crossover (iron ions and protons) through membranes was studied in a complete fuel cell. The single-cell performance of membrane was tested in a cathodic microbial fuel cell (MFC, Biogenerator). The physicochemical properties and membranes fuel cell performance were highly depended on the cross-link density of PVA matrices. Membranes cross-linked with GA for 72 h showed maximum gel content and their peak power density has reached 110 mW cm^{-2} at current density of 378 mA cm^{-2} . Among all, membrane cross-linked for 72 h was studied for continuous long-term stability, which showed consistency for application in MFC.

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1. Introduction

Polymer electrolyte or proton exchange membranes (PEMs) have gained considerable attention due to their applications in energy related fields such as fuel cells and battery systems. The specific applications of fuel cells depend on the type of fuel cell

used. In general, fuel cells are capable of producing power anywhere in the range between a fraction of 1 W to 10 MW scale for automotive, stationary and portable power applications [1]. Basically, a polymer electrolyte membrane fuel cell (PEMFC) creates electrical power from chemical energy by direct continuous conversion of an externally supplied fuel and oxidant. In conventional fuel cells, hydrogen rich oxidizable fuel, hydrogen, methanol, ethanol or formic acid used as proton source, and oxygen used as oxidant. PEMFC can be categorized according to type of electrolyte employed. Among other polymers, PVA has been tested as a cross-

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linked PEM in conventional H_2/O_2 and direct methanol fuel cell (DMFC) applications due to its excellent film forming characteristics and reactive chemical functions favorable for physicochemical modifications [2]. In order to increase mechanical stability and decrease excessive swelling of PVA membranes, cross-linking through chemical treatment was performed. Many reagents explored as cross-linking agents, including glutaraldehyde (GA), provided good control of cross-linking to produce water stable PVA membranes [3–5]. The controlled swelling of membrane may provide porosity for the transport of protons and thereby increase the mobility of protonic charge carrier, leading to slightly increased proton conductivities. Moreover water swollen PVA can be easily doped with H_3PO_4/H_2SO_4 which provides conduction path [6]. Beside that other monomers, oligomers or polymers containing negative charge were often combined with PVA to increase its proton conductivity [2]. Philip and Hsu have systematically studied PVA film membrane preparations through cross-linking by acetalization through GA or periodic acid and by irradiation method [3]. Shen et al. [7] prepared GA cross-linked sulfonated PVA (sPVA) polymer matrix for PEM. Cross-linked sPVA membranes with high degree of sulfonation (DS) exhibited higher conductivity ($1.4 \times 10^{-3} \text{ S cm}^{-1}$) than membranes with a low DS (proton conductivity of $0.96 \times 10^{-3} \text{ S cm}^{-1}$). Zeng et al. [8] reported sol–gel reaction approach between GA and PVA in an aqueous solution of phosphoric acid to fabricate phosphoric acid doped polyGA- H_3PO_4 -PVA (PGA-PVA) hybrid amphibious PEMs. Kang et al. [9] examined blended systems of PVA/polystyrene sulfonic acid-co-maleic acid and GA as cross-linking agent to fabricate PEM for fuel cell.

Generally, cross-linked PVA membranes employed in fuel cell application are produced in composite form [7] because homogeneous PVA film membranes are not mechanically strong enough. A pore-filled composite PEM comprises a porous substrate and a polymer that fills the pores of the substrate. The pore-filled PEMs were prepared either via graft copolymerization from the base polymer (materials), by in situ polymerization or via cross-linking of presynthesized polymers [10]. Functional separation membranes, selective or responsive polymers that swell significantly in water or organic solvents can be mechanically stabilized by entrapment into the membranes pores (with or without anchoring to the wall). In pore-filled polyelectrolyte composite membranes, pore filling materials support proton conductivity while porous support prevents the excessive swelling through the pores walls and provides dimensional stability. For instance, the pore filling composite membranes concept reduced the reactant gas crossover in conventional H_2/O_2 fuel cell [11,12] or methanol crossover in the case of DMFC [13,14] to improve its efficiency. In this respect, various combinations of porous substrate and pore filling polyelectrolyte have used in fuel cells application include: porous polytetrafluoroethylene (PTFE) and polyimide filled with Nafion ionomers, poly(vinyl sulfonic acid co-acrylic acid) or sulfonated polyether sulfone [14–17]; porous PTFE or polyvinylidene fluoride (PVDF) filled with polystyrene sulfonic acid or sulfonated polystyrene [18,19]; and microporous polyethylene impregnated with sulfonated hydrogenated butadiene–styrene block copolymer [20] etc.

The PVA swelling through interaction with aqueous electrolyte such as aqueous sulfuric acid solution allows a protonic charge transfer by the Grötthuss mechanism [21] through hydrogen-bonded sulfuric acid to hydroxyl groups of PVA. The excessive PVA swelling can be controlled by its entrapment into pores of inert substrate membranes. The main goals of the present study included the preparation and characterization of pore-filled composite PEM, which was more suitable for novel microbial fuel cell (MFCs) application. PVA was used as a pore filling material and a track etched PC membrane – as a porous substrate. The PVA was stabilized through cross-linking with GA. The cylindrical pores of the

track etched PC membrane provide short pathways for the protonic charge transfer. The pore-filled PEMs were characterized using Fourier-transform infrared (FTIR) and scanning electron microscopy (SEM). The membrane properties such as water uptake rate, proton conductivity, hydrophilicity and gel content were also determined. Pore-filled PEM described herein were employed in cathodic MFC [22]. Advantageously the MFC uses H_2 gas at anode and biologically produced ferric ion solution at the cathode, and eliminate the use of expensive Nafion PEM and Pt electrocatalyst at the cathode. This paper also shows the performance of the new MEA in a single-cell MFC.

2. Experimental

2.1. Materials

Sample of Elvanol[®] Polyvinyl alcohol (PVA) (Grade: 71–30; 99–99.8% hydrolyzed, Viscosity 27–33 mP S, 4% aqueous solution at 20 °C) was obtained from DuPont (USA). Glutaraldehyde (50 wt.%) was purchased from Caledon Laboratories Ltd. (Georgetown, Canada). Track etched polycarbonate (PC) membranes (pore size of 0.01, 0.1 and 0.2 μm) produced by GE Water & Processes Technologies, were purchased from Midland Scientific, Inc., (Omaha, USA).

2.2. Preparation of pore-filled PEM

The PVA solution (4 wt.%) was prepared in deionized water, and in order to ensure a complete dissolution of PVA, it was heated at 90 °C for 3–4 h. After the solution became clear, it was allowed to cool at room temperature. The solution was filtered off to remove any suspended particles. To prepare pore-filled PEM, the PVA solution was passed through the porous track etched PC membranes using a vacuum filter. The vacuum was applied until the porous membrane became impermeable to the liquid. After impregnation of porous PC membranes with PVA, they were dried for 24 h at room temperature. Further, the dried membranes were dip-coated at room temperature to form a thin layer of PVA on the surface of the PC membrane. The pores of PC membrane were chemically stabilized through cross-linking of PVA using GA as cross-linking agent. Dried PVA membranes were immersed into 0.2 M GA solution (GA solution prepared by diluting 50 wt.% aqueous solution using 0.5 M sodium sulphate solution and pH of solution adjusted to 3 by adding 1 M sulphuric acid solution). After certain time, membranes were lifted from cross-linking bath washed with deionized water to remove any traces of unreacted GA and stored in deionized water.

2.3. Membrane characterization

FTIR spectra of the samples were collected using Nicolet 6700 FT-IR spectrometer (Thermo Scientific, USA). PC, PVA film and pores filled PEMs samples were analyzed using Smart iTR accessory in transmittance mode in the range of wavenumber 4000–600 cm^{-1} with resolution of 4 cm^{-1} .

Top-view and cross-sectional microstructures of PC and PVA pore-filled PC membranes were examined under SEM (HITACHI S-2600N, Japan). The membranes samples were sputter coated with gold and analyzed at 5.0 kV accelerating voltage.

The ionic conductivity of PEMs was determined by a direct current two-point-probe method as described in Ref. [23]. The measuring cell consisted of four compartments. The auxiliary cathode and anode working compartments were used to apply an electrical field. The membrane under investigation was installed between the two central compartments that were separated from the auxiliary compartments by anion and cation exchange

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