Polymer 55 (2014) 6102–6109

Contents lists available at ScienceDirect

Polymer

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

Air-breathing microbial fuel cell with enhanced performance using nanocomposite proton exchange membranes

Mohammad Mahdi Hasani-Sadrabadi [a, b], Erfan Dashtimoghadam [c], Seyed Nasireddin Saeedi Eslami [d], Ghasem Bahlakeh [e, f], Mohammad Ali Shokrgozar [d], Karl I. Jacob [a, g, *]

[a] G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA
[b] Department of Biomedical Engineering, Amirkabir University of Technology, Tehran, Iran
[c] Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran
[d] National Cell Bank, Pasture Institute of Iran, Tehran, Iran
[e] Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran
[f] Department of Engineering and Technology, Golestan University, Aliabad Katool, Iran
[g] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA

ARTICLE INFO

Article history:
Received 5 April 2014
Received in revised form
8 September 2014
Accepted 14 September 2014
Available online 22 September 2014

Keywords:
Air-breathing microbial fuel cells
Sulfonated poly(ether ether ketone)
Nanocomposite membranes

ABSTRACT

This work aims to improve the performance of air-breathing microbial fuel cells (MFCs) through using hydrocarbon polymer based nanocomposite proton exchange membranes. Accordingly, nanocomposite membranes based on sulfonated poly(ether ether ketone) (SPEEK) and montmorillonite (MMT) were investigated for such an application. Although the incorporation of MMT into SPEEK membranes resulted in reduced oxygen permeability as well as proton conductivity, but the overall selectivity was found to be improved. MFC tests revealed that using the optimized nanocomposite membrane (SPEEK-70/MMT-3 wt %) results in a considerably higher open circuit voltage (OCV) compared to the corresponding neat membrane. Moreover, it was found that the SPEEK-70/MMT-3 wt% membrane is able to provide about 40% more power output than Nafion®117. On the account of high proton conductivity, low oxygen permeability, high electrochemical performance, ease of preparation and low cost, hydrocarbon based nanocomposite PEMs could be considered as promising electrolytes to enhance the performance of MFCs.

1. Introduction

Microbial fuel cells (MFCs) are generally considered as bio-reactors, wherein a variety of chemicals such as fatty acids, alcohols, sugars, proteins, and cellulose in an aqueous medium like in wastewaters, are oxidized to produce electricity [1–3]. During the past years, MFCs have attracted considerable attention owing to their broad range of applications such as wastewater treatment [4], space applications [5], biosensors [6], and power generation [7]. The MFC technology has emerged as a sustainable energy resource as it addresses two main challenges of the modern societies: green energy supply and wastewater management [5].

Like other types of fuel cells, MFCs are composed of an anode, a cathode, and an electrolyte. The electrons produced by oxidation of the substrate via bacterial catalysis can be transferred to the anode through various routs including, electron mediators or shuttles [8,9], direct electron transfer through a physical/electrical contact between the bacterial cell membrane and the anode substrate [5,9], or by means of nanowires [10].

Proton exchange membranes (PEMs) are considered as the key component of polymer electrolyte membrane fuel cells. An ideal PEM not only acts as an electrolyte to conduct protons to the anode side, but also separates the anode and cathode chambers and prevent leakage of the substrate and electron to cathode and oxygen to the anode [11,12]. Although the single-chamber MFC without a PEM has been reported to produce higher power density [13], but on the other hand the oxygen and substrate diffusions in

* Corresponding author. School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA. Tel.: +1 404 894 2541; fax: +1 404 894 8780.
E-mail address: karl.jacob@ptfe.gatech.edu (K.I. Jacob).

http://dx.doi.org/10.1016/j.polymer.2014.09.033
0032-3861/

the absence of a separator were found to reduce the columbic efficiency and bioelectrocatalytic activity of the anode microorganisms [14].

One of the most common PEM materials is Nafion®, from DuPont, which is widely used in hydrogen fuel cells as well as direct methanol fuel cells (DMFCs) and MFCs [5]. Nafion® membranes offer high proton conductivity at optimal water contents as well as long-term thermal/chemical stability in oxidative conditions [15]. However, in the case of MFCs, Nafion® aside from its high cost shows high oxygen permeability, which results in a reduced columbic efficiency [16] and catalyst deactivation. Hence, this study aims to improve the performance of air-breathing microbial fuel cells (MFCs) through using an alternative nanocomposite PEM.

Various PEMs have been developed so far as alternatives for Nafion®-based membranes [17–20]. Among them, PEMs based on partially sulfonated poly(ether ether ketone) (SPEEK), owing to their high chemical, thermal and mechanical stability, high proton conductivity and low cost, are considered as suitable candidates for fuel cell applications [21–23]. Compared to Nafion® membranes, nanoscale phase separation of hydrophobic and hydrophilic domains in SPEEK matrices occurs in a lower extent. Such an observation is attributed to the lower acidity of the sulfonate groups, absence of fluorinated groups, and the higher mechanical stiffness of its aromatic backbone, which lead to an order of magnitude lower permeability compared to Nafion® membranes [24]. On the other hand, the comparatively lower acidity of sulfonic acid groups on SPEEK chains results in lower proton conductivity compared to perfluorosulfonated polymers. Hence, higher substitution of sulfonate groups should be achieved to provide high proton conductivity. However, increasing the degree of sulfonation (DS) is limited by the extra swelling and excessive permeability of polar molecules [21–23]. In the view of this, incorporation of inorganic fillers is considered as an effective approach to notably reduce permeability through the creation of tortuous pathways [25–30]. As oxygen was found to have a disturbing effect on the function of anaerobic bacteria (e.g. *Escherichia coli*), the current research is relied on the hypothesis that introducing tortuous pathways against permeation of oxygen as well as cations and anions, could leads to a higher electrochemical performance of the designed MFCs.

It has been recently reported by our research group that SPEEK/montmorillonite nanocomposite PEMs are able to provide higher performance and electrochemical properties in DMFCs compared to Nafion®117 [21–23]. Correspondingly, the effect of SPEEK/montmorillonite as a nanocomposite PEM on performance of an air-breathing microbial fuel cell using *E. coli* bacteria will be investigated in the present study.

2. Experimental section

2.1. Membrane preparation

Sulfonation process of PEEK (PolyScience, Inc., USA) was carried out according to the previously reported procedure [21–23]. Sulfonated PEEK samples with various degrees of sulfonation were dissolved in N,N-Dimethylacetamide (DMAc, Merck Chemical Co., Germany). Organically modified montmorillonite clay (MMT, Cloisite™ 15A, Southern Clay Products Inc., USA) was suspended in DMAc at room temperature via stirring for 2 h, ultra-sonication for an hour and then mixed with the SPEEK solutions. The mixtures obtained were then ultra-sonicated for half an hour, stirred for 8 h at 80 °C and then concentrated. The resultant suspensions were cast on glass plates, incubated at room temperature overnight, 70 °C for 8–10 h, and then 120 °C for 12 h. Subsequently, the membranes were boiled in 3 wt% hydrogen peroxide (Merck Chemical Co., Germany) for half an hour, and washed in boiling deionized water. Membranes were then boiled in 1 M sulfuric acid for half an hour to convert to H-form, and washed several times with deionized water. Nafion®117 membrane (E.I. DuPont de Nemours Co.) was also treated through the same procedure of boiling and washing, for the sake of comparison.

2.2. Membrane characterization

The oxygen permeability of membranes (P) was determined using the constant pressure/variable volume method at 25 °C via a laboratory made test cell according to the following equation:

$$P = \frac{Q \cdot l}{A \cdot (p1 - p2)}$$

where, Q is flow rate of the permeate molecules through the membrane, l is the membrane thickness, A is the effective membrane area, $p1$ and $p2$ are the absolute pressures at the feed and permeate sides, respectively. The permeability coefficient is expressed in Barrers units ($\times 10^{10}$ cm (STP)^3 cm cm^{-2} s^{-1} cm Hg^{-1}).

Proton conductivity measurements were performed via a conductivity cell, which has been designed for a four point probe measurement to obtain bulk conductivity of membranes. The cell was set into a humidity chamber at 95% RH and 25 °C, for at least 3 h before conductivity measurements of the fully hydrated membranes (with water or TSB). The degree of sulfonation (DS), ion exchange capacity (IEC) and TSB/water uptake were measured in accordance with the previous reports [21–23].

2.3. Bacterial strain and cultivation

To obtain a culture, *E. coli* Top10F (Invitrogen) was maintained on LB agar (AppliChem GmbH, Darmstadt, Germany) with 12.5 mg/L tetracycline. Five milliliter Tryptic Soy Broth (TSB, BD. Bioscience)-17 gr/L tryptone, 3 gr/L soytone, 2.5 gr/L glucose, 5 gr/L NaCl, 2.5 gr/L K_2HPO_4 - and 12.5 mg/L tetracycline were inoculated with a single colony and incubated aerobically at 37 °C on a rotary shaker (100 rpm) overnight. One milliliter of the cell suspension was then added to 100 ml TSB with tetracycline and incubated like the previous stage, but under more vigorous agitation (250 rpm). After 2.5 h, the optical density was checked by spectrophotometer (Eppendorf) at 600 nm at 10 min time intervals until reach to 0.5 A. The experiments were then started promptly. In addition to TSB, the MFC was contained with methylene blue (0.05 mM concentration) and glucose as the mediator and fuel, respectively.

2.4. MFC design

Electrochemical performance of the fabricated membranes was investigated using a laboratory made air-breading single-chamber double cell MFC at 30 °C. As shown in Fig. 1, the MFC is consisted of a proton exchange membrane sandwiched between two carbon cloth electrodes (TGP-H-120 Toray). The cell was composed of 316 stainless steels as current collectors and flow fields. Silicone rubber sheets were used to seal the internal sections. The Pt-black was used as the cathode electro-catalyst, which was applied via the catalyst painting technique [20]. In brief, the catalyst was mixed with Nafion® solution (5 wt% dispersion, E.I. DuPont de Nemours Co.) and several drops of glycerol (Merck chemical Co.) as suspension/painting agent. Then, the provided suspension was brushed directly (4 mg cm^{-2}) onto the dry membrane, and hot-pressed at 100 °C for 90 s. Finally, the prepared MEAs were boiled in a dilute acidic solution and washed several times with deionized water.