Renewable Energy 102 (2017) 77–86

Contents lists available at ScienceDirect

Renewable Energy

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

Characterization and performance study of phase inversed Sulfonated Poly Ether Ether Ketone – Silico tungstic composite membrane as an electrolyte for microbial fuel cell applications

Prabhu Narayanaswamy Venkatesan, Sangeetha Dharmalingam*

Department of Mechanical Engineering, Anna University, Chennai, 600 025, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form
6 October 2016
Accepted 15 October 2016
Available online 17 October 2016

Keywords:
SPEEK
Silicotungstic acid
Entrapment
Cation transport
Oxygen crossover
MFC

ABSTRACT

Hybrid composite membranes possess the desired properties than that of the pristine polymeric membranes for fuel cell applications. Phase inversion method was used to entrap silicotungstic acid (STA) particles in Sulfonated Poly Ether Ether Ketone (SPEEK) membranes as a source of protons having a high protonic conductivity at room temperature (0.02–0.1 S/cm). The physico-chemical properties of the hybrid membranes were characterized by SEM-EDX, line scanning, 3D non-contact profilometer, FTIR and XRD techniques. These membranes showed better ion exchange, proton conductivity values and were tested in single chamber microbial fuel cell (SCMFC). In addition, these membranes show decreased oxygen crossover and transport of cations other than protons. Among the various weight percentage (2.5%, 5%, 7.5% and 10%) of STA prepared composite membranes, 7.5% STA + SPEEK showed the highest power density of 207 mWm^{-2} compared to that of commercial Nafion 117 (47 mWm^{-2}) in the same setup of SCMFC. Overall, the composite membranes proved to be excellent candidates as electrolytes for Microbial Fuel Cell (MFC) applications.

1. Introduction

Polymer electrolyte membrane based fuel cells are popular due to their hazard-free electricity generation potential. Polymer electrolyte membranes include proton and hydroxyl ion conducting membranes that are widely used in proton and alkaline fuel cells respectively. MFCs are a relatively new bio-electrochemical systems, which utilize microorganisms as catalysts for electricity generation from waste biomass and essentially work on the same principle as that of the hydrogen fuel cell [1,2].

An MFC consists of an anode and a cathode chamber, which are separated by a separator, preferably a polymer membrane. Anode chamber contains degradable organic wastes with bacterial inoculum while the cathode chamber contains oxidizing agents such as potassium ferricyanide, potassium permanganate or simple air facing cathode without a chamber [3,4].

Membranes such as Nafion and separators like J-cloth, glass fiber are also utilized as separators in MFCs. The high oxygen and substrate crossover along with the potential for accumulation of cations (such as Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}) other than the proton are some of the factors that determine the efficiency of the membranes during MFC operation [5,6]. The efficiency of J-cloth is observed to be highly influenced by the formation of biofilm over the surface which affects the oxygen crossover. While, at the same time the increased substrate loss due to the consumption by microorganisms with lower columbic efficiency is observed and its biodegradability is one of the limitations to its practical application [7]. To overcome the problems related to membranes, membraneless microbial fuel cells were introduced. However, membraneless MFC also shows certain shortcomings such as higher oxygen and substrate diffusion, which lower the coulombic efficiency and bio-electrocatalytic activity of the anode microorganisms [7]. On the other hand, although MFCs using separators (membranes) add cost to the system, they hold their own significance in terms of increasing the effective operation of the system by minimizing substrate and oxygen crossover. Researchers, mainly focus on the improvement of membrane properties for their efficient performance in MFC which includes the preparation of hydrocarbon based homopolymeric and composite membranes to overcome the drawbacks of commercial fluorinated membranes [8–11].

Water retention properties of many inorganic fillers like TiO_2,

* Corresponding author.
E-mail address: sangeetha@annauniv.edu (S. Dharmalingam).

http://dx.doi.org/10.1016/j.renene.2016.10.027
0960-1481/

SiO_2, zeolite and functionalized fillers are used to either modify or to improve the properties of polymer electrolytes which influence the performance of chemical as well biofuel cells [12–15]. Heteropoly acids (HPA) are known to be strong Bronsted acid having a protonic conductivity in the range of 2×10^{-2} Scm^{-1} along with high thermal stability and are also used as filler for various polymer matrices [16] for displaying efficient fuel cell performance. However, the water soluble property of HPA is its short come in fuel cell application at high temperatures, which would lead to its leaching out from the polymer matrix during fuel cell testing [17]. Sun et al., in their study showed that a viscous mixture of silicotungstic acid with phosphoric acid as a filler into the polymer matrix improved the chemical and thermal stability of the membrane [18]. Tian et al. showed that the conductivity of Nafion/Silicotungstic Acid (STA) composite membrane remained same before and after its immersion in water. However, this Nafion/STA composite membrane showed a decrease in conductivity when subjected to boiling water treatment, due to the washout of STA particles from the membrane surface. Such problems do not arise in MFC, since it works in aqueous medium at room temperature. In addition, in proton exchange membranes the presence of sulfonyl groups in the membrane prevents the dissolution of STA from the membrane, due to the synergistic effect between the sulfonyl group ($-SO_3H$) and the STA group, thus reducing the loss of STA from the membrane [19]. These overall properties of STA ensure that it can be used as filler in separators for their utility in an MFC application.

The phase inversion method is used widely in the formation of porous polymer nanocomposite membranes with entrapped fillers for various applications [20]. In this method, the attachment of nanoparticles on the pore surface of membranes bestow the advantages of better accessibility of immobilized nanoparticles to reactants in the permeate flow and utilize the properties of nanoparticles. Phase inverse type prepared membrane shows superior physical and electrochemical properties compared with that of cast samples [21].

In this study, the phase inversion method was used to prepare the STA + SPEEK composite membranes, in which the STA fillers were immobilized or entrapped within the SPEEK matrix and to utilize their favorable properties like the high hydration ability and conductivity properties with an aim at improving the properties of the base SPEEK membranes having an oxygen mass transfer coefficient an order lesser than that of Nafion. Consequently, by employing this method, the electrochemical performance in terms of proton conductivity of the SPEEK based membrane was improved.

This study elaborates the preparation; properties of STA entrapped SPEEK composite membranes and the real scale application of the membrane in Single Chamber Microbial Fuel Cell (SCMFC).

2. Materials and method

Analytical grade Poly Ether Ether Ketone (PEEK) (150 XF, Mol. Wt. 1,00,000) (Victrex), Concentrated sulfuric acid (Conc. H_2SO_4, assay 98%, Merck), D – Glucose (99.5%, Sigma-Aldrich), Ethanol (SRL), Nutrient medium (Sigma-Aldrich) and *N*-Methyl Pyrrolidone (NMP, 99%) (SRL), STA (SRL), Concentrated Hydrochloric acid (Conc. HCL, assay 35%, Merck) were commercially procured and were used without any further purification.

2.1. Sulfonation of PEEK and composite membrane preparation

PEEK polymer was sulfonated as per our previous reported method [22]. A weighed amount of PEEK (5 g) was dissolved in concentrated sulfuric acid (90 ml) and magnetically stirred for 5 h at room temperature. After 5 h, the reaction mixture was poured into ice cold water and the sulfonated form of PEEK (SPEEK) was obtained in the form of white precipitate. The degree of sulfonation (DS) of the obtained SPEEK was 50%. It was then washed with deionized water for several times until the pH became neutral and dried overnight at 80 °C. It was then dissolved in a suitable quantity of NMP (2 g in 25 ml) and the viscous solution was spread onto a clean glass plate. Phase inversion membranes were then obtained by slowly dipping the glass plate into concentrated hydrochloric acid (35%). The membranes were then washed with deionized water to remove any excess acid if present. The membranes were dried at 80° C for 24 h.

SPEEK with DS of 50% was chosen for this study, because a higher percentage of sulfonation with higher water uptake may result in reduced stability. Apart from the stability of the polymer, increasing the number of sulfonyl groups will also increase the oxygen crossover through the sulfonated membranes which is an important factor in deciding the performance of membranes in MFC application.

2.5%, 5%, 7.5% and 10% Wt. % of STA with hot air oven dried SPEEK ionomer were taken for the preparation of composite membranes. To prepare the composite membrane, the desired amount of STA was added into the SPEEK–NMP solution, stirred and degassed by ultrasonication. The prepared mixture was spread onto a glass plate to result in a composite membrane of thickness approximately 0.019 cm. Prior to analysis, each membrane was pretreated to remove organic and metallic impurities [22]. The prepared composite membranes were characterized using the methods which are reported in our previous studies [13] and are given below in detail.

2.2. Instrumental characterizations

2.2.1. Fourier transform infrared spectroscopy (FTIR)

The prepared composite membranes were characterized using ATR- Fourier transform infrared spectrometer (Alpha T-Bruker Optics) for the presence of functional groups and their interaction with the composites. The membranes were scanned in ATR mode from the wave number of 400 cm^{-1} – 4000 cm^{-1}.

2.2.2. SEM

The surface morphology, EDX-line scan of the composite membranes were studied using VEGA3 TECSCAN at an accelerating voltage of 10 kV and a resolution of 10 μm. Prior to SEM analysis, all the samples were coated with gold by sputtering.

2.2.3. Surface roughness

The surface roughness of all the membranes were studied using a 3D non-contact profilometer (Taylor Hobson hardness tester) and the respective average roughness (Ra) values were calculated using TalyMap Platinum 5.1.1.5374 software.

2.2.4. Water uptake

Water uptake by the composite membranes was determined from the change in the weight of the composite membranes before and after hydration. All the membranes were dried well in a hot air oven and then taken for the study. The percentage of water absorption was calculated using the relation given below.