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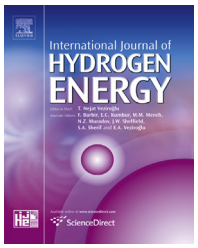

Composite membrane containing graphene oxide in sulfonated polyether ether ketone in microbial fuel cell applications

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ABSTRACT

In this study, a single layer graphene oxide is successfully synthesized and used as a nano-filler in a self-fabricated sulfonated polyether ether ketone (SPEEK) to make a composite proton exchange membrane, graphene oxide/SPEEK (GO-SPEEK). The properties of GO-SPEEK, Nafion® 117 and SPEEK are then compared to ascertain their selectivity to proton transport compared to both water and oxygen. GO-SPEEK was found to have the highest selectivity with a water uptake of 85.4%, proton conductivity of 1.48×10^{-3} S cm^{-1} and oxygen diffusion coefficient of 1.154×10^{-6} cm^2 s^{-1}. During tests in Microbial Fuel Cells (MFCs), the MFC system with Nafion® 117 membrane produces the highest maximum power density (1013 mW m^{-2}) followed by the MFCs with GO-SPEEK (902 mW m^{-2}) and SPEEK (812 mW m^{-2}) membranes. On the other hand, the MFC with GO-SPEEK membrane produces the highest coulombic efficiency (16.88%). The high efficiency and comparable maximum power density which is produced by the MFC with GO-SPEEK membrane, shows that GO-SPEEK membrane is a promising alternative membrane to replace the expensive Nafion® 117 as a separator in the MFC.

Introduction

Fuel cell technology is undeniably a promising and reliable alternative energy technology for use in recent years and in the future. The Microbial Fuel Cell (MFC), an emerging fuel cell technology had received significant attention in recent years from the scientific community all over the world as an alternative source of energy because of its promising dual capability of producing electricity while simultaneously treating wastewater [1]. However, the commercialization of the MFC is hampered by its low power density [2,3] and relatively high

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production cost due to the costly Nafion membrane used as the separator and the expensive platinum catalyst used in the cathode [4,5]. Hence, the search for a new cheaper membrane that has a comparable performance to Nafion as a separator in MFC is badly needed [5].

The main functions of the membrane as a separator in the MFC is to prevent oxygen crossover from cathode to anode that would otherwise destroy the anaerobic condition in the anode [6] and passage of substrate from anode to cathode that would otherwise fouls the cathode [7,8] while maintaining high proton diffusion from anode to cathode [9,10].

Nafion® 117, a perfluorinated membrane is the most popular membrane used in fuel cell technology because of its desirable properties like high proton conductivity [11] and good mechanical strength [12]. Besides being costly [13], another major drawback of this membrane is its oxygen and substrate crossover [14]. Most commercialized cation exchange membranes have been found to have high ohmic resistance [15], while anion exchange membranes have high substrate permeability [16]. This prompted some researchers to employ membraneless technology for MFC. However, membraneless MFCs have been reported to have unfavourable oxygen reduction reaction in the cathode due to severe biofouling [7,8,17] that significantly reduce its coulombic efficiency [18–20]. Recent studies have been focused on utilizing composite membranes because of their better performance and lower price. The sulfonated polyether ether ketone/polyether sulfone (SPEEK/PES) [21] and ferric oxide nano-particle/polyether sulfone (Fe_3O_4/PES) [22] have shown better performance than Nafion 117® membrane in MFC applications. Modified Nafion® membranes, such as activated carbon nanofiber/Nafion®117 (ACNF/Nafion® 117) [9] and Nafion® 112/polyaniline [23] composite membranes, have also produced higher power densities than their original Nafion® membrane in MFC.

In this paper, the performance of a novel nano-composite membrane called graphene oxide/sulfonated polyether ether ketone (GO-SPEEK) membrane was studied specifically for MFC applications.

SPEEK polymer was used as the membrane's polymer matrix, because it has high proton conductivity, good mechanical strength, good thermal properties, chemical inertness, and most importantly, it is cheaper than Nafion® 117 membrane [24–27]. Graphene oxide (GO), is a compound that consists of carbon, oxygen, and hydrogen atoms [28]. Its modified form (sulfonated graphene oxide) was reported to have been used as a nano filler for nano-composite membranes [29–32]. However, only one study reported on graphene oxide blended in poly(ethylene oxide) polymer matrix for low temperature PEMFC [28]. Graphene oxide have low electronic conduction, but good proton conductivity because of the presence of hydroxyl, carboxylic, and epoxy groups in the hydrophilic region of GO [28,29]. In addition, the sp^2 carbon layer present in the hydrophobic region of GO can help to increase the mechanical strength of the membrane because of its strong covalent bonding [29]. In this research, a self-synthesized GO-SPEEK membrane was characterized and its properties were compared with those of Nafion® 117 and pure SPEEK membranes. The performance of these membranes in MFC applications in terms of power density, COD removal and coulombic efficiency were then compared.

Experimental

Sulfonation of PEEK polymer and determination of the degree of sulfonation

Fifteen grams of PEEK was dissolved in 300 ml of 95–98% concentrated sulphuric acid and the solution was stirred vigorously using a mechanical stirrer. The reaction was carried out at room temperature for 6 h to obtain a homogeneous solution [33], then heated to 55 °C, and continued to be stirred for 5 h. The reaction was stopped by pouring the homogeneous solution into a large excess of ice water under mechanical stirring. The white SPEEK polymer precipitate was filtered out and flushed with distilled water until the pH is neutral.

The existence of sulfonic acid group in the SPEEK polymer was identified and characterized by Nicolet 5700 FT-IR (Thermo Electron, USA) and ^1H nuclear magnetic resonance (FT-NMR ADVANCE 111 600 MHz with Cryoprobe) spectroscope (Bruker, Karlsruhe, Germany) to obtain its Degree of Sulfonation (DS).

Synthesizing and characterization of graphene oxide

Graphene oxide was synthesized using a modified Hummers method [34]. 100 ml of 95–98% concentrated H_2SO_4, 1.5 g $NaNO_3$ and 3 g of graphite flake were added into a beaker that was immersed in an ice bath. The solution underwent mechanical stirring. 9 g of $KMnO_4$ was then slowly added into the solution, whereby the solution's temperature did not exceed 20 °C. After the dissolution of $KMnO_4$, the solution was removed from the ice bath and stirred at room temperature for a further 12 h 150 ml of deionized water was then slowly added to dilute the viscous solution, and stirred for a further 12 h. After the dilution, 30 wt% H_2O_2 was added, followed by 100 ml 5 wt% HCl (each addition required stirring for 2 h). The solution was then centrifuged, and the supernatant was discarded to leave only the precipitate. The precipitate (graphite oxide) was washed with 5 wt% HCl several times, followed by deionized water using centrifuge, until the wash solution became neutral. The graphene oxide (GO) solution was obtained by dispersing a specific amount of graphite oxide in deionized water and ultrasonicated for 10 min until a homogeneous solution was obtained. This solution was centrifuged, at 1500 rpm for 10 min, to remove the unexfoliated graphite oxide.

The graphite flakes and synthesized graphene oxide were analyzed using the FT-IR to identify the bonding structures of the sample by measuring the absorption spectra due to the stretching, bending and vibration of various types of chemical bonding present in the sample. They are also viewed in a Transmission Electron Microscopy (TEM- Hitachi HT 7700, Japan) to determine the presence of exfoliated GOs and their size. The thickness of the exfoliated GO was measured using Atomic Force Microscopy (NTEGRA PRIMA AFM-NT-NDT,