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Sulfonated poly ether ether ketone with different degree of sulphonation in microbial fuel cell: Application study and economical analysis

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ARTICLE INFO

Article history:
Received 8 March 2015
Received in revised form 22 September 2015
Accepted 6 October 2015
Available online 23 October 2015

Keywords:
Proton exchange membrane
Nafion 117
SPEEK
Cost efficiency analysis
Power generation

ABSTRACT

A microbial fuel cell (MFC) is a device for the simultaneous treatment of wastewater and the generation of electricity with the aid of microorganisms as a biocatalyst. Membranes play an important role in the power generation of microbial fuel cells. Nafion 117, the most common proton exchange membrane (PEM), is expensive and this is the main obstacle for commercialization of MFC. In this study, four kinds of sulphonated poly ether ether ketone (SPEEK) with different degrees of sulphonation (DS) referred to hereafter as SPEEK 1 (DS = 20.8%), SPEEK 2 (DS = 41%), SPEEK 3 (DS = 63.6%), and SPEEK 4 (DS = 76%), were fabricated, characterized and applied in an MFC. The membranes were characterized by thermogravimetric analysis TGA) and differential scanning calorimetry (DSC) and their morphologies were observed by scanning electron microscopy (SEM). The degree of sulphonation was determined by nuclear magnetic resonance (NMR). Then the membranes were applied to the MFC system. The results indicated that the power produced by MFC with SPEEK 3 (68.64 mW/m^2) was higher than with the other SPEEK membranes while it was lower than with Nafion 117 (74.8 mW/m^2). SPEEK3 also had the highest chemical oxygen demand removal (91%) and coulombic efficiency (26%) compared to other SPEEK membranes. The cost evaluation suggests that application of SPEEK 3 is more cost effective than applications of the other types of SPEEK and Nafion 117, due to its high power density generation per cost.

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http://dx.doi.org/10.1016/j.ijhydene.2015.10.029

Introduction

Recently, due to the depletion of fossil fuels and environmental issues associated with the use of conventional fuels, fuel cells have begun to attract attention due to their low emissions of pollutants and high efficiency. Microbial fuel cells (MFCs), as a novel technology, convert the chemical energy in organic compounds into electricity and biohydrogen with the aid of microorganisms as the biocatalyst. Generally, MFC is a device that simultaneously produces energy and treats the wastewater [1,2]. Also, MFC can be applied for the bioremediation of some pollutants [3]. MFC is similar to any other fuel cell or battery, and consists of two parts (an anode and a cathode), separated by a proton exchange membrane (PEM) [4,5]. The performance of MFC depends on several factors, including the type of electrode, the cathode catalyst, the PEM, the distance of the electrodes, the microorganisms, etc. However, among all these factors, the membrane plays one of the most significant roles as it separates the anode from the cathode, and must support the transfer of protons from the anode to the cathode while inhibiting the transfer of media from the anode to the cathode and blocking the crossing over of oxygen from the cathode to the anode [6]. One of the major obstacles to the commercialization of MFC is the high capital cost of the PEM, which covers about 40% of the expenses for MFC [7,8]. Numerous researches have been carried out with regard to the different types of PEMs (nanocomposites, ultrafiltration, etc.) in MFCs, but due to complications in the MFC system and the existence of several factors, a proper membrane has not been found yet or is not commercial [9,10].

Recent researches on developing suitable and cost efficient PEMs in fuel cells have focused on aromatic polymers such as polyimide (PI), polybenzimidazole (PBI) and polyether ether ketone (PEEK) composite membranes. Among the various polymeric membranes with diverse mechanical, thermal, and electrical properties, PEEK has been shown to be one of the most promising due to its long term stability, cost efficiency, and performance [11]. Studies have found that SPEEK has good thermal stability, high proton conductivity and mechanical stability. All of these properties have been affected by degree of sulphonation of the membrane [12].

Although there have been myriad studies about the various types of membranes which have been used as PEMs in MFCs, not much study has been done as to the application of sulphonated polyether ether ketone (SPEEK) in MFCs. However, it has been used widely in other types of fuel cells and as nanofiltration membranes for wastewater treatment [13,14]. This study focused on effect of degree of sulphonation of membranes in performance MFCs. In 2012, Ghasemi et al. [9] developed and applied activated carbon nano fibre/Nafion as a PEM in MFC. It produced a power that was 1.5 times more than the power produced by Nafion 117, the traditional PEM in MFC. Also, in another study, Rahimnejad et al. [15] fabricated Fe_3O_4/PES nanocomposite membranes and compared the performance of those with Nafion 117. This PEM also produced a power that was 1.3 times more than that of Nafion 117. However, the big obstacle to using these types of membranes in MFC is their porous nature which allows the passing of media from the anode to the cathode and also oxygen from the cathode to the anode, thus disturbing the performance of MFC in the long term [16].

This study is aimed at improving the performance of MFC by using different sulphonated polyether ether ketones (SPEEK) as the PEM with different degrees of sulphonation to maximize the power generation and efficiency of the MFC and furthermore, the cost effectiveness of the different types of SPEEK for use in microbial cells is investigated.

Materials and methods

Synthesis of SPEEK

For the preparation of SPEEK, 20 g of PEEK powder (Goodfellow Cambridge Limited, UK) was dissolved slowly in 500 ml of 95–98% concentrated sulphuric acid (R & M Chemicals, Essex, UK).

This solution was stirred vigorously until the entire PEEK was dissolved completely. Next, the homogenous solution was continuously and thoroughly stirred at a controlled temperature of 80 °C for 1, 2, 3, and 4 h (SPEEK 1, SPEEK 2, SPEEK 3, and SPEEK 4, respectively) to get the SPEEK with different degrees of sulphonation. Each of the SPEEK solutions was then poured into a large excess of ice water to precipitate the SPEEK polymer. The solid was then collected by filtering the solution through a Whatman filter paper. Finally, the SPEEK was dried at 70 °C to remove any remaining water before use [17].

Determination of DS

The degree of sulphonation was measured by 1H Nuclear Magnetic Resonance (FT-NMR ADVANCE 111 600 MHz with Cryoprobe) spectroscopic analysis (Bruker, Karlsruhe, Germany). Before taking the measurement, the SPEEK was dissolved in dimethyl sulphoxide (DMSO-d_6). The DS can be calculated by the following equation,

$$\frac{DS}{S-2DS} = \frac{A1}{A2} \quad (0 \leq DS \leq 1) \tag{1}$$

where S is the total number of hydrogen atoms in the repeat unit of the polymer before sulphonation, which is 12 for PEEK, $A_1(H_{13})$ is the peak area of the distinct signal, and A_2 is the integrated peak area of the signals corresponding to all other aromatic hydrogens. To calculate the DS percentage (DS %), the value for the DS has to be multiplied by 100 [18].

Fabrication of membranes

Ten grams of different kinds of SPEEK were dissolved in 90 g of N-methyl-2-pyrrolidone (NMP) to make 10 wt% of pure solution of SPEEK. The solution was stirred for 24 h. After that it was cast onto a glass plate by using a casting knife [19]. The membranes were then dried in a vacuumed oven (for making the membrane uniform). The membranes were separated from the glass plate by immersing them in water. They were kept in deionised water before use [20].