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Influence of sulfonated SiO_2 in sulfonated polyether ether ketone nanocomposite membrane in microbial fuel cell

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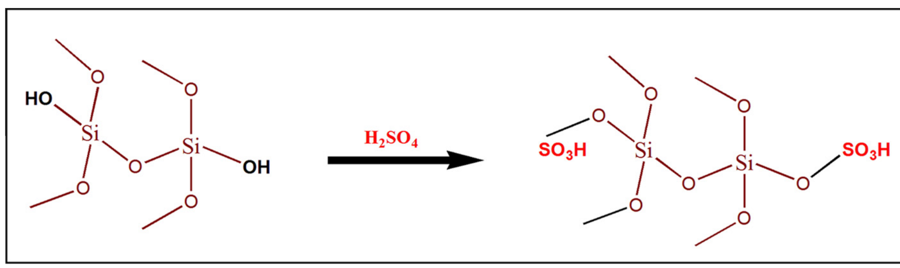
HIGHLIGHTS

- Use of SiO_2-SO_3H as additive in SPEEK enhanced IEC, proton conductivity and MFC performance.
- Improved performance of composite membranes was due to the sulfonation effect of SiO_2–SO_3H particles.
- K_O of composite membranes was lower than that of SPEEK and Nafion.
- 7.5% SiO_2–SO_3H composite membrane delivered 3-fold higher power output than Nafion 115.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cell (MFC) is a bioreactor for simultaneous electricity generation and wastewater treatment. Modified nanocomposite membranes based on sulfonated poly ether ether ketone (SPEEK) and sulfonated SiO_2 (SiO_2–SO_3H) were fabricated and evaluated in a microbial fuel cell configuration. Proton conductivity, water uptake, ion exchange capacity (IEC), oxygen crossover, internal resistance and MFC performance of SPEEK membrane, SPEEK incorporated with silica (SPEEK-SiO_2) composite membrane and SPEEK incorporated with various percentages of sulfonated silica composite membranes (S-2.5%, S-5%, S-7.5% and S-10%) were studied and compared. The results revealed that the incorporation of sulfonated SiO_2 improved the proton conductivity of the SPEEK membrane effectively and exhibited the highest peak power density of 1008 mW m^{-2} for S-7.5%, when compared to 680 mW m^{-2} and 802 mW m^{-2} obtained for SPEEK and SPEEK-SiO_2 membranes respectively in a single chambered microbial fuel cell (SCMFC). In comparison to Nafion 115 (320 mW m^{-2}) the composite membrane delivered more than 3-fold higher power density in the same MFC setup. The oxygen mass transfer coefficient (K_O) of the composite membranes decreased with the increase in the sulfonated SiO_2 content of the membrane. The internal resistance for S-7.5% and SPEEK membranes were measured to be 46 Ω and 71 Ω respectively. The improved performance of the composite membranes was due to the higher proton conductivity of the introduced SiO_2–SO_3H that facilitated an effective proton transfer in the membrane.

1. Introduction

MFC is a device that can generate electricity from waste or organic matter by using microorganisms as active biocatalyst. MFCs have interested many researchers because they provide the possibility of directly harvesting electricity from different substrates such as organic wastes and renewable biomasses. In fact, simultaneous bioelectricity generation and wastewater treatment are considered as one of the most important applications of MFC [1–8]. Although a number of factors, such as MFC design, electrode materials, types of fuels, and working conditions affect a MFC's

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performance, it is the membrane which has high impact on the MFC performance that mainly affects the power density. Nafion 115 membrane is the widely used proton exchange membrane (PEM) in MFCs, in spite of the existence of a number of problems associated with it such as high cost ($\$1500\ m^{-2}$), oxygen crossover, substrate loss, cation transport and accumulation rather than protons [9–14]. The major problem with MFC is the oxygen diffusion into the anode compartment, which (i) consume the electrons in the anode compartment, thereby reducing the coulombic yield, (ii) increase the substrate loss by promoting the growth of aerobic respiration facultative bacteria and (iii) inhibit the growth of obligate anaerobes [14].

Use of organic–inorganic composite membranes for fuel cell applications have been widely studied by scientists due to the potential enhancement of the water retention properties and proton conductivity at higher temperature [15]. Such inorganic materials used in composite membranes include SiO_2, TiO_2, ZrO_2, Al_2O_3 and so on. Silica/Nafion® composite membranes were prepared in various ways and evaluated in high temperature PEMFCs [16].

In most cases the metal oxide based composite membranes showed better performance at higher temperatures only. But at lower temperatures such composite membranes reduced the proton conductivity when compared to the pristine membrane. Hence, the hygroscopic property did not always lead to a desired performance improvement. Many researchers have reported that the proton conductivity of composite membranes was remarkably reduced due to the incorporation of these non-proton-conductive hygroscopic metal oxides at low temperatures [15,17–21].

An MFC is operated at 30 °C under fully wet condition. Hence an increased proton conductivity of the membrane is required at room temperature. Based on this, in the present work, a proton conductive acidic metal oxide additive, sulfonated SiO_2 was incorporated into SPEEK to fabricate the composite membranes. To retain the hydrated form of the membrane, metal oxides have been used to provide a path for proton transport. Whereas, when sulfonated metal oxides are used, the SiO_2 groups of the sulfonated metal oxides not only create a path for proton transport but also act as vehicle due to its negative charge.

Wang et al. prepared Nafion/PTFE, Nafion/PTFE/SiO_2, Nafion/PTFE/SiO_2–SO_3H and Nafion/PTFE/SiO_2-1,3 propane sultone (PS) composite membranes and showed higher power density for the metal oxide sulfonated composites (Nafion/PTFE/SiO_2–SO_3H and Nafion/PTFE/SiO_2-1,3-PS) than the unsulfonated metal oxides containing composites (Nafion/PTFE and Nafion/PTFE/SiO_2) in PEMFC [22]. Ke et al. also prepared Nafion sulfonated SiO_2 composite membranes by sol gel method and showed lower membrane resistances than the unsulfonated Nafion/SiO_2 [23].

All the above composite membranes reported in literatures were prepared with Nafion for high temperature PEMFCs only. In the reported work, sulfonated silica was used as the proton conducting additive and the composite membranes (S-2.5%, S-5%, S-7.5% and S-10%) were analyzed by FTIR, SEM, EDX and XRD. Water uptake, IEC, ionic conductivity and oxygen mass transfer coefficient (K_O) of the composite membranes were also determined. The composite membranes containing sulfonated metal oxides were evaluated in MFC and the performances in terms of power and coulombic efficiency have been discussed and compared with SPEEK, SPEEK-SiO_2 and Nafion 115 membranes.

2. Materials and methodology

2.1. Preparation of sulfonated SiO_2

SiO_2 nanoparticles with a size of 25 nm were purchased from Sigma Aldrich. The sulfonated SiO_2 was prepared using sulfuric acid according to the method reported by Wang et al. [22], Ke et al [23] and Lin et al. [24]. One gram of SiO_2 particles was added to 20 ml methanol solution containing 15 ml of 0.5 M sulfuric acid. This solution was ultrasonicated for one hour and was allowed for evaporation at 100 °C for 24 h. This finally resulted in SiO_2–SO_3H white powder. The final product, sulfonated silica (SiO_2–SO_3H) was obtained by drying the solution at 100 °C for 24 h.

2.2. Preparation of membranes

Synthesis of sulfonated PEEK (SPEEK) was carried out as described in earlier reports [10]. In a typical experiment, 10 g of dry PEEK powder (Victrex, England) was dissolved in 150 ml of sulfuric acid under nitrogen atmosphere. The reaction mixture was allowed to proceed for 8 h with continuous stirring at 60 °C. The reaction was terminated with ice.

To prepare the composite membranes, desired amount of prepared SiO_2–SO_3H or pure SiO_2 was added into the SPEEK/NMP solution (1 g/15 ml), which was stirred mechanically and then degassed by ultrasonication. The concentration of SiO_2–SO_3H in the mixture varied from 0 to 10 wt.% while 5 wt.% of pure SiO_2 on SPEEK matrix was prepared for comparison purpose. The prepared mixture was slowly poured onto a glass dish in an amount that would give a thickness of 120 μm for the formed composite membrane. The glass dish was then placed on the levelled plate of a vacuum oven for 24 h at 60 °C to evaporate the solvent. The membranes obtained were designated as given in Table 1 according to the weight percentage of the filler added. All the membranes were pre-treated by boiling in H_2O_2 (30% v/v) and deionized water, followed by soaking in 0.5 M H_2SO_4 and then deionized water, each for 1 h.

2.3. Instrumental characterization

2.3.1. FT-IR spectral analysis

FT-IR spectra of SiO_2, SiO_2–SO_3H, SPEEK, SPEEK-SiO_2 and various composite membranes were recorded from 500 cm^{-1} to 4000 cm^{-1} using an Alpha Bruker FTIR spectrophotometer. The spectrum was measured in the transmittance mode with a resolution of 2 cm^{-1}.

2.3.2. SEM–EDX analysis

Scanning electron microscopy (SEM) (JEM-5600LV) and EDX techniques (Oxford instruments X-ray Microanalysis) were used to analyze the elemental distribution of the metal oxides on the surface of the composites. The morphology of the various composite membranes was also studied.

2.3.3. XRD analysis

X-ray diffraction (XRD) is a technique that is used to identify the crystalline and amorphous materials. In the present study, XRD patterns of membrane samples were recorded using "X" Pert Pro diffractometer. The scanning angle was 1–80° with a scanning rate of 2° per minute.

Table 1
Membrane codes.

Membrane code	% Composition of SPEEK: SiO_2/SiO_2–SO_3H
SPEEK	100:0
SPEEK-SiO_2	95:5
S-2.5%	97.5:2.5
S-5%	95:5
S-7.5%	92.5:7.5
S-10%	90:10