Chemical Engineering Journal 289 (2016) 442–451

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# Nanocomposite membranes based on sulfonated polystyrene ethylene butylene polystyrene (SSEBS) and sulfonated $SiO_2$ for microbial fuel cell application

Ayyaru Sivasankaran [a], Dharmalingam Sangeetha [b], Young-Ho Ahn [a,*]

[a] Department of Civil Engineering, Yeungnam University, Gyeongsan 38541, South Korea
[b] Department of Mechanical Engineering, Anna University, Chennai, India

## HIGHLIGHTS

- The use of S-$SiO_2$ as additive in SSEBS enhanced the IEC, proton conductivity and MFC performance.
- S-$SiO_2$ have a larger negative zeta potential than $SiO_2$.
- Improved performance of the composite membranes was due to the sulfonation effect of S-$SiO_2$ particles.
- $K_O$ of the composite membranes was lower than that of SSEBS and Nafion.
- The 7.5% $SiO_2$ composite delivered 4-times higher power density than Nafion 117.

## ARTICLE INFO

*Article history:*
Received 22 September 2015
Received in revised form 7 December 2015
Accepted 23 December 2015
Available online 5 January 2016

*Keywords:*
Microbial fuel cell
SSEBS
Sulfonated $SiO_2$
Proton conductivity
Oxygen permeability
Power density

## ABSTRACT

A new sulfonated $SiO_2$ (S-$SiO_2$) and sulfonated polystyrene ethylene butylene polystyrene (SSEBS) nanocomposite was used to fabricate a proton exchange membrane single chamber microbial fuel cells (SCMFCs). SSEBS containing various concentrations of S-$SiO_2$ (2.5%, 5%, 7.5%, and 10%) was prepared. The nanomaterials and nanocomposite membranes were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. The nanocomposite membranes were also examined for their ion exchange capacity (IEC), water uptake, proton conductivity and oxygen crossover. The MFC with the SSEBS-S-$SiO_2$ membrane (7.5%) exhibited a higher peak power density of $1209 \pm 17$ mW $m^{-2}$ than other composite membranes. In the SSEBS and SSEBS-$SiO_2$ membrane systems, the peak power density was $680 \pm 13$ mW $m^{-2}$ and $852 \pm 11$ mW $m^{-2}$, respectively. The composite membrane showed 4 times higher power density than the Nafion 117 membrane ($290 \pm 7$ mW $m^{-2}$). Overall, the composite membrane (particularly at S-$SiO_2$ –7.5%) is a suitable technology in the MFC process because of its high proton conductivity imparted by S-$SiO_2$.

## 1. Introduction

A microbial fuel cell (MFC) is a bio-electrochemical reactor that produces electricity through the microbial oxidation of biodegradable organic substrates under anaerobic conditions [1–2]. MFCs have attracted considerable attention in recent years because of their promising dual capability of producing electricity and treating wastewater simultaneously as well as providing the possibility of directly harvesting electricity from different substrates [1–6]. Scale-up is essential for the commercial application of MFC technology, particularly for wastewater treatment. On the other hand, the scale-up of MFCs significantly reduces the power density, resulting in high production cost due to the use of expensive Nafion membranes and platinum catalysts [7,8]. The principle of a proton exchange membrane used in MFC is that, it should facilitate the transfer of protons from the anode to cathode while at the same time inhibit the transfer of other materials, such as the fuel (substrate) and the electron acceptor (oxygen). A Nafion membrane is considered the most widely used proton exchange membrane (PEM) in MFCs, despite the 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 MFCs is the oxygen diffusion into

---

* Corresponding author. Tel.: +82 10 3283 3511.
*E-mail address:* yhahn@ynu.ac.kr (Y.-H. Ahn).

http://dx.doi.org/10.1016/j.cej.2015.12.095
1385-8947/

the anode compartment, which (i) consumes electrons in the anode compartment, thereby reducing the coulombic yield, (ii) increases the substrate loss by promoting the growth of aerobic respiration facultative bacteria and (iii) inhibits the growth of obligate anaerobes [14].

Surface modification of nanoparticles in composite with polymers is an effective way to improve its dispensability in an organic polymeric matrix, enhancing the properties of the composite materials. Various organic–inorganic composites have been synthesized with enhanced properties using different polymers and nanofillers [15–25]. In that order, several studies have demonstrated the potential use of organic- inorganic composite membranes in fuel cells owing to their high water holding capacity, causing viable proton conductivity at high temperatures (60–80 °C) [26,27]. Inorganic materials (such as $SiO_2$, $TiO_2$, $ZrO_2$, $Al_2O_3$, etc.) have been introduced ideal candidates at high temperatures in composite membranes for use in proton exchange membrane fuel cells (PEMFCs), but these composite membranes often leads to reduced proton conductivity compared to the pristine membrane at low temperatures (30 °C) [26–34]. Therefore, in the MFC process, an increase proton conductivity of the membrane (in the refuse of metal oxides) through the use of acidic additives (sulfonated $SiO_2$) to enhance their performance can be recommended because they have been operating under fully wet conditions at 30 °C. In this study, silica ($SiO_2$) was used due to its good physical, chemical and thermal properties. Silica was typically used in the form of nano-particles, which provides high surface area and excellent chemical stability. The addition of hydrophilic sulfonated SiO2 fillers into the polymer matrix served to reduce the glass transition temperature ($T_g$) and the crystallinity while at the same time increased the amorphous phases of the polymer matrix, as well its ionic conductivity.

A previous study, reported that the use of SSEBS as a PEM in MFCs could provide a much higher power density ($600 \pm 14$ mW $m^{-2}$) than Nafion ($290 \pm 7$ mW m) [13]. The SSEBS could overcome the disadvantages of oxygen leakage from the cathode to anode and substrate loss, that are associated with a Nafion membrane. Therefore, the present approach aimed to use sulfonated silica as a proton conducting additive in SSEBS. Accordingly, composite membranes with different concentrations of sulfonated $SiO_2$ were prepared and characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Water uptake, ion exchange capacity (IEC), ionic conductivity, and oxygen mass transfer coefficient ($K_0$) of the composite membranes were also determined. The composite membranes containing sulfonated metal oxides were evaluated in the MFC with the index of power and coulombic efficiency, and compared with the unsulfonated SSEBS-$SiO_2$ as a control.

## 2. Materials and methodology

### 2.1. Materials

The monodisperse tri-block co-polymer, PSEBS having a number-average molecular weight (Mw) of 89,000, was purchased from Sigma–Aldrich (USA). Silica (10–15 nm) was purchased from Sigma Aldrich (USA) with the purity of 99%. Other chemicals like chloroform, methanol, THF, TBP and sulfuric acid 98%, were purchased from Sisco Research Laboratory (SRL) Pvt. Ltd., India. All were of analytical grade and were used as received. Twenty percent of Pt on Vulcan XC-72 purchased from Arora-Mathey Pvt. Ltd., India was used as a cathode catalyst. Carbon cloth was obtained from Cabot carbon Inc., Germany.

### 2.2. Preparation of sulfonated $SiO_2$

$SiO_2$ nanoparticles, 25 nm in size, were purchased from Sigma Aldrich. The sulfonated $SiO_2$ was prepared using sulfuric acid using the method reported by Cheng et al. [24,34,35] and Ayyaru and Dharmalingam [36]. One gram of $SiO_2$ particles was added to 20 ml of a methanol solution containing 15 ml of 0.5 M sulfuric acid. The solution was ultrasonicated for 1 h and allowed to evaporate at 100 °C for 24 h. This finally resulted in S-$SiO_2$ white powder.

### 2.3. Preparation of membrane

The polystyrene ethylene butylene polystyrene (SEBS) was sulfonated with chlorosulphonic acid (CSA). The procedure was adopted from the reported article [13,37]. The weighed (10 g) SEBS polymer sample was taken in a round bottom flask and dissolved in a measured quantity of chloroform to obtain a clear polymer solution, which was then allowed to cool in an ice bath. Then 5 ml of tributyl phosphate (TBP) (to moderate the reaction) followed by the required amount of CSA (6 ml) was added drop wise over a period of time with vigorous stirring in a nitrogen atmosphere. The reaction was carried out under ice cold conditions for 3 h. After 3 h, the reaction was quenched by adding low molecular weight aliphatic alcohol to the reaction mixture and stirring was continued for another 2 h to obtain a uniformly mixed product. The solution mixture obtained was poured into a glass plate and the solvent was allowed to evaporate to yield a dry sulfonated polymer. To remove the excess acid from the product, the dry polymer was washed several times with deionized water until a neutral pH was reached. The purified product was dried at 60 °C for 1 day.

### 2.4. Preparation of composite membranes

To fabricate the composite membranes, an appreciable amount of S-$SiO_2$ or $SiO_2$ preparation was added to the SSEBS/THF (tetrahydrofuran) solution (2 g/15 ml), stirred mechanically, and degassed by ultrasonication. The addition of S-$SiO_2$ to the mixture was varied from 0 to 10 wt.% (Table 1 and Fig. 1). The $SiO_2$ with 7.5 wt.% on the SSEBS matrix was prepared for comparison. The prepared mixture was poured slowly onto a glass dish in an amount that would give a thickness of 180 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. Table 1 lists the membranes obtained according to the weight percentage of filler added. All the membranes were pre-treated by boiling (100 °C) in $H_2O_2$ (30% v/v) and deionized water, followed by soaking in 0.5 M $H_2SO_4$ and then in deionized water, each for 1 h.

### 2.5. Characterizations

The FT-IR spectra (Alpha Bruker) of $SiO_2$, S-$SiO_2$, SSEBS, SSEBS-$SiO_2$, and various sulfonated composite membranes were recorded from 500 $cm^{-1}$ to 4000 $cm^{-1}$ in transmittance mode with a resolution of 2 $cm^{-1}$. The chemical state and composition of the sul-

**Table 1**
Membrane codes.

| Membrane code | Mass ratio of SSEBS:$SiO_2$/S-$SiO_2$ |
|---|---|
| SSEBS | 100:0 |
| SSEBS-$SiO_2$ 7.5% | 92.5:7.5 |
| SSEBS-S-$SiO_2$ 2.5% | 97.5:2.5 |
| SSEBS-S-$SiO_2$5% | 95:5 |
| SSEBS-S-$SiO_2$ 7.5% | 92.5:7.5 |
| SSEBS-S-$SiO_2$ 10% | 90:10 |