ABSTRACT

The use of fossil fuels, especially petroleum, in recent years has accelerated a global energy crisis. Furthermore, the combustion of fossil fuels releases more CO₂ to the atmosphere and causes global climate change. Therefore, a carbon-neutral, sustainable energy sources as alternatives to fossil fuel is needed to alleviate the global energy crisis and climate change. A number of research and development programmes is focused in this area, especially on microbial fuel cells. Microbial fuel cells (MFCs) are interesting for many researchers in the world because they provide the possibility of directly harvesting electricity from different substrates such as organic waste and renewable biomass. In fact, simultaneous bioelectricity generation and waste water treatment is considered as one of the most important applications of MFC.

In the present work, polymer electrolyte membranes were fabricated from sulfonated poly ether ether ketone (SPEEK) and sulfonated poly styrene ethylene butylene poly styrene (SPSEBS) for MFC applications. Inorganic fillers (TiO₂ and SiO₂) were sulfonated using sulphuric acid and used for the preparation of respective composite membranes. Their efficiencies were compared with composite membrane containing corresponding non sulfonated inorganic fillers. Additionally the SPEEK was used as a biosensor in single chamber microbial fuel cell (SCMFC) to determine the biochemical oxygen demand (BOD) matter present in artificial wastewater (AW)

Polyether ether ketone (PEEK) was sulfonated to sulfonated poly ether ether ketone (SPEEK) using sulphuric acid and evaluated as a proton exchange membrane (PEM) in a SCMFC. SCMFC fabricated with SPEEK
membrane produced higher power density than Nafion 117. The oxygen mass transfer coefficient \((K_0)\) was one order lesser for SPEEEK when compared to Nafion 117 thereby reducing substrate loss thus increasing coulombic efficiency (CE). From this investigation the SPEEEK could be a suitable PEM for improving the efficiency of MFCs.

The modified nanocomposite membranes based on SPEEEK with sulfonated TiO_2 and sulfonated SiO_2 have been fabricated and evaluated in microbial fuel cell. The metal oxide particles and its composite membrane were characterized by XRD, FT-IR, SEM and EDS techniques. Proton conductivity, water uptake, IEC, oxygen crossover, MFC performance and internal resistance were studied and compared with SPEEEK membrane. The water absorption, IEC and ionic conductivity were increased with the increase in the content of sulfonated metal oxides. The oxygen mass transfer coefficient \((K_0)\) of nanocomposite membranes decreased with incorporation of the sulfonated metal oxides.

The SPEEK-TiO_2-SO_3H membrane (7.5 %) exhibited the highest peak power density of 1202 ± 12 mWm\(^{-2}\) than the power density of 766 ± 6 mWm\(^{-2}\) and 676 ± 7 mWm\(^{-2}\) obtained for SPEEEK-TiO_2 and SPEEEK membranes respectively. The SPEEK-SiO_2-SO_3H delivered the maximum power density of 1008 ± 17 mWm\(^{-2}\) when compared to the SPEEK-SiO_2 (802 ± 11mWm\(^{-2}\)) membrane and SPEEEK (680 ± 13 mWm\(^{-2}\)) membrane in SCMFC.

In comparison to Nafion (300 ± 7 mWm\(^{-2}\)), both SPEEK-TiO_2-SO_3H and SPEEK-SiO_2-SO_3H composite membranes delivered more than 3-fold higher power density. The increased performance for the composite membranes was attributed to the increased acidic sites of the sulfonated metal oxide particles that enhanced the proton conductivity of the composite membrane. Among the sulfonated composite membranes, SPEEK-TiO_2-SO_3H
showed superior MFC performance than SPEEK-SiO$_2$-SO$_3$H. In case of non-sulfonated composites, the SPEEK-SiO$_2$ showed better performance than SPEEK-TiO$_2$ membrane which was due to the more water absorption properties of SiO$_2$.

SPSEBS cation exchange membrane was successively prepared viz. sulfonation using chlorosulfonic acid and the SCMFC performance was evaluated. SPSEBS membrane exhibited low internal resistance than Nafion 117. The oxygen mass transfer coefficient ($K_o$) was one order lesser for SPSEBS than the Nafion 117 which reduced the substrate loss and increased the coulombic efficiency.

In the case of SPSEBS based composite membranes, the concentration of the sulfonated metal oxide content was varied from 2.5% to 10%. The sulfonation of metal oxide and its composite membranes were characterized by XRD, FT-IR, SEM and EDX techniques. To authenticate the sulfonation of metal oxide in nanocomposite membranes, the proton conductivity, water uptake, IEC, oxygen crossover, MFC performance and internal resistance were analysed. The sulfonation of metal oxide increased the number of sulfonic groups (-SO$_3$H), which significantly increased the proton conductivity of the composite membrane. These sulfonated composite membranes showed higher performance than non-sulfonated one. The improved performance was attributed to the introduction of TiO$_2$-SO$_3$H particles, whose high proton conductivity and good water adsorbing/retaining function, effectively increased the proton transfer in the composite membrane. The membrane with SPSEBS-TiO$_2$-SO$_3$H showed the improved MFC performance than SPSEBS-SiO$_2$-SO$_3$H. This was due to higher order to sulfonation in TiO$_2$ when compared to SiO$_2$. However the non sulfonated SPSEBS-SiO$_2$ showed better MFC performance over SPEEK-TiO$_2$ due to greater water absorption capability of silica.
SPEEK membrane was also used in SCMFC to determine the biochemical oxygen demand (BOD) matter present in artificial wastewater (AW). The biosensor produced a good linear relationship with the BOD concentration up to 650 ppm when artificial wastewater was used. This sensing range was higher than that of Nafion®. SPEEK exhibited one order lesser oxygen permeability than Nafion, resulting in low internal resistance and substrate loss, thus improving the sensing range of BOD. The system was further improved by making a double membrane electrode assembly (MEA). Double MEA provided a larger surface area for electrochemically active bacteria that actively oxidized larger amount of substrate from the AW, in a way increasing the electron mass transfer and reducing the response time (80 min) and hydraulic retention time (HRT) of the biosensor.

Collectively, it may be inferred that the hydrocarbon based proton exchange membranes (SPEEK and SPSEBS) used in MFC are efficient, eco-friendly and a cheaper alternate for the Nafion. The enhanced performance was due to the low oxygen diffusion property of hydrocarbon membranes. The sulfonated inorganic fillers were used to fabricate composite membranes and such composite membranes showed good proton conductivity which is very important for consideration as an electrolyte in microbial fuel cells. Good compatibility was observed for all the composite membranes towards MFC applications. With these investigations, it may be concluded that these composite membranes could act as an excellent replacement for commercially available cation exchange membrane (Nafion 117) in MFC due to an appreciable reduction in the oxygen permeation and higher performance.