Water Science & Technology

IWA PUBLISHING

Water Science & Technology Vol 84 No 10-11, 3388 doi: 10.2166/wst.2021.467

Evaluation of power generation and treatment efficiency of dairy wastewater in microbial fuel cell using TiO_2 – SPEEK as proton exchange membrane

D. Vidhyeswari [a], A. Surendhar [b] and S. Bhuvaneshwari [a,*]

[a] Department of Chemical Engineering, National Institute of Technology Calicut, Kozhikode 673601, India
[b] Department of Food Technology, TKM Institute of Technology, Kollam, India
*Corresponding author. E-mail: sbuvana@nitc.ac.in

DV, 0000-0001-5620-1934; AS, 0000-0003-1900-3642; SB, 0000-0002-1090-3356

ABSTRACT

The aim of this study is to synthesise SPEEK composite proton exchange membrane with the addition of TiO_2 nanofillers for microbial fuel cell application. SPEEK composite membrane with varying weight percentage of TiO_2 (2.5, 5, 7.5 and 10%) was prepared to study the effect of TiO_2 concentration on membrane performance. Synthesized composite membranes were subjected to various characterization studies such as FT-IR, XRD, Raman spectroscopy, TGA, UTM and SEM. Physico-chemical properties of membrane such as water uptake capacity, ion exchange capacity and thickness were also analyzed. 5% TiO_2 – SPEEK composite membrane exhibited the higher water uptake capacity value and Ion exchange capacity value of 31% and 1.71 meq/g respectively. Performance of the MFC system with TiO_2 – SPEEK membranes were evaluated and compared with the pristine SPEEK and Nafion membrane. 5% TiO_2 – SPEEK membrane produced the higher power density (1.22 W/m^2) and voltage (0.635 V) than the other membranes investigated. Efficacy of MFC in wastewater treatment was evaluated based on the chemical oxygen demand (COD), total organic carbon content and turbidity. Biofilm growth over the surface of the electrodes was also analyzed using scanning electron microscopy.

Key words: anaerobic, biofilm, chemical oxygen demand, dairy wastewater, microbial fuel cells, power generation

HIGHLIGHTS

- Use of TiO_2 – SPEEK composite membrane as alternate for the Nafion 117.
- Energy generation from dairy wastewater was investigated using dual chambered MFC.
- Low cost membrane.
- Green energy.
- TiO_2 – SPEEK can be used to overcome drawbacks of Nafion 117.

1. INTRODUCTION

The present world is in search for an alternative sustainable energy resource due to faster depletion of the existing fossil fuels. Fuel cells are considered to be a promising electrochemical device in generating power in the current scenario (Singh *et al.* 2010). There are various types of fuel cells based on the electrolyte employed, catalyst used and the process parameters. Among them, microbial fuel cells is one type of electrochemical system wherein microbes act as a catalyst. Organic/inorganic matter and chemical compounds contained in the waste resources are the fuel/energy source for these fuel cells. Moreover, the reaction is taking place in ambient temperature condition compared to elevated thermal conditions in hydrogen fuel cells. Apart from generating power, microbial fuel cells proved to have the potential to simultaneously treat the wastewater by utilizing the chemical energy present in them. Thus microbial fuel cells perform two activities (power generation and wastewater treatment) at the instance which is most demanded for the current environmental situation (Santoro *et al.* 2017; Tiwari *et al.* 2019).

These microbial fuel cells consist of an anodic chamber and cathodic chamber, which are partitioned by the proton exchange membrane. Wastewater containing organic matter/inorganic matter was usually considered as substrate for the cell (Peeva *et al.* 2014). Microbes present in the wastewater oxidize the organic matter present in them resulting in formation of protons and electrons. Protons migrate through the PEM to the cathode chamber and get reduced with oxygen to form water. On the other hand electrons pass through the conductive electrode in the anode chamber to cathode chamber via external circuit thereby generating the electricity (Gavimath *et al.* 2012; Yazdi *et al.* 2016). Effectiveness of the microbial fuel cells in power generation and wastewater treatment is dependent on various parameters such as electrodes, microbes and proton exchange membrane. Proton exchange membrane is of greater importance in a microbial fuel cell compared to other parameters (Vidhyeswari & Bhuvaneshwari 2018). India is the largest producer and consumer of milk and milk products. It also has a large number of dairy industries throughout the country. Wastewater discharged from dairy industries in India also poses environmental issues to natural water resources. Hence, to deal with such situations, an effective wastewater treatment method is necessary. Since dairy wastewater is easily biodegradable, various biochemical methods, namely membrane reactor and anaerobic sludge blanket reactor, have been used for treatment purposes. Even though biological processes are economic processes, MFC has an additional advantage of generating power during wastewater treatment. In this study, dairy wastewater was taken as the fuel for the MFC system since it contains various proteins, carbohydrates and fat content (Faria *et al.* 2017).

Most of the studies on microbial fuel cells were carried out using the commercially available PEM Nafion. Nafion was considered in the MFC application based on the properties which are advantageous for the operation in the microbial fuel cell. Few drawbacks associated with the Nafion and its higher cost paved the way to synthesise cost-effective PEM (Kaur *et al.* 2020). In recent years, sulfonated poly (ether ether ketone) (SPEEK) was identified as a cost effective polymeric membrane in fuel cell applications. Properties of the SPEEK membrane were improved by incorporating filler material to increase its efficiency in MFC applications (Ji *et al.* 2021). TiO_2 was proved to improve the electrochemical properties of SPEEK polymer. Thus, in this study, TiO_2 incorporated SPEEK membrane was synthesized and characterized using various characterization techniques. Synthesized membranes were evaluated for their physico-chemical properties and compared with the pristine SPEEK and Nafion membrane. Performance of the synthesized membrane in power generation and wastewater treatment was also evaluated in an MFC system.

2. MATERIALS AND METHODS

2.1. Materials

The materials used in this study were purchased commercially from different sources. PEEK (Krishna Polymers, Chennai), Concentrated H_2SO_4 (Merck), D-glucose (Hi Media), Ethanol (Sigma Aldrich), N-methylpyrrolidone (NMP) (SRL), Titanium (IV) oxide (TiO_2) (Sigma Aldrich), carbon cloth (Sainergy Fuel Cell India Private Limited) and all other chemicals were cast-off without any additional purification. Nafion117 (Sainergy Fuel Cell India Private Limited) were used as outdated membranes to target the concerts of recently synthesized membranes.

2.2. Membrane preparation

Sulfonation of PEEK was done by using concentrated sulfuric acid as sulfonating agent. 7.5 gram of PEEK was dissolved in 140 ml of concentrated sulfuric acid and magnetically stirred for 8 hours. After 8 hours, the reaction mixture was poured into an ice bath (prepared from deionized water) to terminate the sulfonation reaction and the resulting SPEEK obtained was in the form of white precipitate. The SPEEK was washed several times with deionized water until it reached neutral pH. The resulting polymer was dried at 80 °C for 2 hours followed by overnight drying at 110 °C under vacuum. One gram of SPEEK was dissolved in 10 ml of NMP for 6 hours under magnetic stirrer to have a homogenous polymer solution. The solution was cast onto a clean flat glass and dried in a vacuum oven at 80 °C for 24 hours. After drying, the membrane was peeled off (Mohtar *et al.* 2011).

For the preparation of TiO_2 nanocomposite membrane, the desired quantity of TiO_2 was added in the SPEEK NMP solution and sonicated for one hour. 2.5%, 5%, 7.5% and 10% of TiO_2-SPEEK membrane were prepared. Nafion117 was pretreated by boiling in distilled water followed by 3% H_2O_2 and 0.5M H_2SO_4 at 80 °C for one hour each. The pre-treated membrane is stored in distilled water (Dou *et al.* 2008; Xin *et al.* 2014).

2.3. Synthetic dairy wastewater preparation

It is prepared by mixing Glucose (90 mg), Yeast (10 mg), Milk powder (1,500 mg), Starch (5 mg), Ammonium chloride (50 mg), Di potassium hydrogen phosphate (25 mg), Di hydrogen potassium phosphate (15 mg), Magnesium sulphate (80 mg), Calcium carbonate (30 mg) in 1 litre of distilled water. The pH was adjusted to 7 before introducing into

MFC setup. The characteristics of synthetic wastewater were found to be as follows: Chemical oxygen demand (COD): 2,418 mg/L; Biological oxygen demand (BOD): 1,185 mg/L; Total organic carbon (TOC): 724 ppm; Turbidity: 409 NTU (Asha & Elakkiya 2014).

2.4. Isolation and enrichment of microorganisms

Dairy wastewater was collected from MILMA, Kunnamangalam, Kozhikode district of Kerala. Mixed culture of anaerobic organisms were isolated and used for MFC. Organisms were introduced into 100 ml of Thioglycollate broth and kept in an incubator with mechanical shaker. After 24 hours, the medium was centrifuged to collect the pellets. The pellets were dissolved in 5 ml of distilled water and used along with anolyte in MFC. Since pure cultures require high controlled operating environment for isolation and maintenance, such kinds of culture are not preferred. The usage of mixed culture instead of pure culture has led to reduced expenditure in the current experimental setup (Logan *et al.* 2006; Du *et al.* 2007; Patra 2008; Nimje *et al.* 2012).

2.5. MFC construction and operation

Dual-chambered MFC was fabricated using an acrylic material with two equal-volume rectangular chambers (5 cm × 5 cm × 10 cm) as shown in Figure 1. These chambers had a total/working volume of 200/150 ml. Carbon cloth (30 wt% wet proofed) electrodes were dipped in the respective compartments. The copper wires were connected to electrodes with a multimeter. 145 ml of synthetic dairy wastewater and 5 ml of organism prepared were taken in the anodic chamber. An equal amount of distilled water (150 ml) was taken in the cathodic chamber. The anodic chamber was purged with N_2 to maintain anaerobic conditions. The slow mixing of around 150 rpm was provided using a magnetic stirrer (REMI 1MLH). An external load of 100 Ω resistor was applied to form a closed circuit (Vidhyeswari & Bhuvaneshwari 2018). The MFC set up is operated at room temperature.

2.6. Membrane characterization

2.6.1. Water uptake

Water uptake for SPEEK and nanocomposite membranes was studied by the weight change in membranes before hydration and after hydration. 1 cm * 1 cm sized membrane was dipped in deionized water for 24 hours at room temperature.

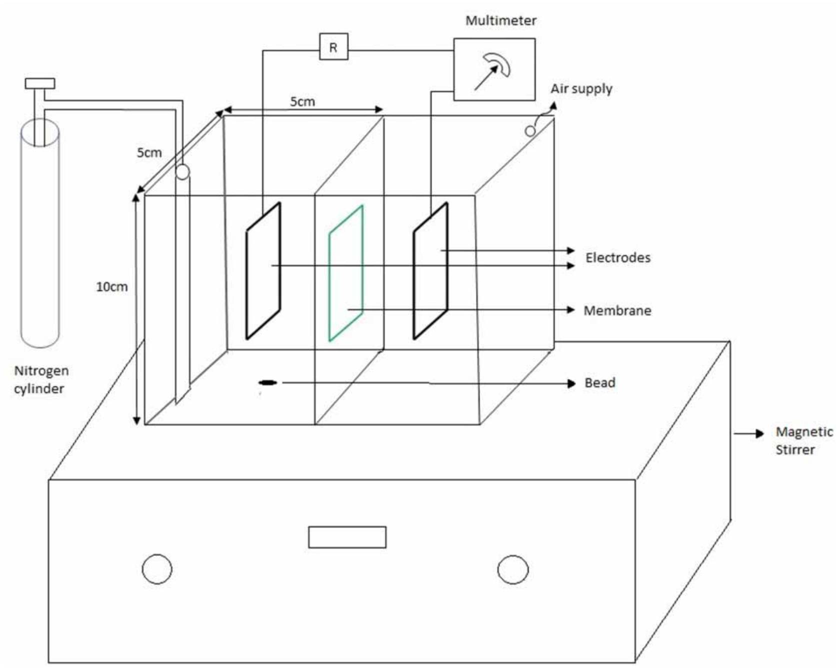

Figure 1 | Schematic diagram of the dual chambered microbial fuel cell.

Membrane was taken out of the deionized water and the excess surface water was removed to find the wet weight of the membrane. The membrane was dried at 100 °C in a vacuum oven for 12 hours and the weight was noted. Water absorption percentage was calculated by using the following equations.

$$Water\ absorption\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where, W_{wet} – Weight of wet membrane. W_{dry} – Weight of dry membrane after drying in vacuum oven at 100 °C for 12 hrs (Xin *et al.* 2014).

2.6.2. Ion exchange capacity (IEC)

Ion exchange capacity is defined as the measure of the capability of an insoluble material that undergoes displacement of ions formerly attached and roughly incorporated into its structure because of opposite charge ions present in the neighboring solution. In general, IEC is calculated from the back titration method.

$$IEC = \frac{\text{Titre value(in ml)} \times \text{Normality of } Na_2CO_3}{\text{Weight of dry polymer membrane(in g)}} \text{meq/g} \quad (2)$$

2.6.3. Morphology studies of electrode

Surface morphologies of the electrode used in the MFC system was analyzed to evaluate the biofilm growth using scanning electron microscopy (SEM). A small portion of carbon cloth (after shut down of experiments) was taken and washed five times with phosphate buffer saline. It was fixed with 2.5% glutaraldehyde and kept undisturbed for 24 hours in order to stabilize the surface and intracellular structures. The fixed samples were washed three times with sodium phosphate buffer and were dehydrated in a series of graded alcohols (10, 30, 50, 80 and 100% of ethanol). All specimens were dried and coated with a thin coating of gold. Microbes in the biofilm usually differ with the change in the wastewater type (Fratesi *et al.* 2004).

2.6.4. Instrumental characterization of membranes

The prepared nanocomposite membranes were characterized for their functionality through various characterizations. Composite membranes were analyzed for the presence of functional groups using Fourier transform infrared spectrophotometer (FT-IR) (Agilent Technologies – Carry 630) to identify the polymer and filler functionality. The presence of TiO_2 was further confirmed through Raman Spectroscopy (Horiba Labram). The crystallinity of materials was determined by X–ray diffraction (XRD) (Rigaku Miniflex 600) methods. Thermal stability of materials can be evaluated by Thermo gravimetric analysis (TGA) (Hitachi STA7200). Tensile strength of the properties can be determined by universal testing machine (UTM) (Shimadzu AG-X plus 10 kN). Morphological studies were performed through Scanning Electron Microscope (SEM) (Hitachi SU6600) analysis to identify the uniform scattering of the filler in the polymer matrix. The thickness of the membrane was calculated using the Digimatic Micrometer (Mitutoyo). The electrochemical activity of the electrodes in dairy wastewater was evaluated using cyclic voltammograms (CV) (CH Instruments, CHI760).

2.7. Analytical measurements and calculations

A digital multimeter (V&A TECH MAS830) has been used to record cell voltage over time. The current flow (I), the power (P), the current density (I_D), and the power density (P_D) were estimated from the following equations (Nam *et al.* 2017):

The current was calculated using Ohm's law

$$I = \frac{V}{R} \quad (3)$$

where, I is the current (mA), V is the voltage (mV) and R is the external resistance (U).

Power (P) was calculated as,

$$P = IV \quad (4)$$

Power density (W/m^2) was calculated as,

$$P_D = \frac{P}{A} \tag{5}$$

where, A is the surface area of the electrode.

Current density (A/m^2) was calculated as,

$$I_D = \frac{I}{A} \tag{6}$$

3. RESULTS AND DISCUSSIONS

3.1. Water uptake and ion exchange capacity

A unique characteristic of the SPEEK-based membrane is the proton transfer by means of the Grotthuss mechanism, which states that a proton diffuses via the water molecule present it. Thus, water uptake capacity is considered as one of the important property for the SPEEK-based membranes. To check the hygroscopic property of the prepared composite SPEEK membrane, water uptake capacity was measured. Water uptake values of the prepared SPEEK membrane with varying concentrations of TiO_2, pristine SPEEK membrane and Nafion membrane are presented in Table 1. Maximum water uptake capacity of 31% was obtained for the 5% TiO_2 – SPEEK. Results show that water uptake value increased from 2.5% to 5% TiO_2 – SPEEK membrane. It is also found that values are high compared to the pristine SPEEK and Nafion. Increased water uptake capacity is attributed to the incorporation of TiO_2 nano particles, which provides more acidic sites for the water absorption (Ayyaru & Dharmalingam 2013). Further, increase in the TiO_2 concentration to 7.5 and 10% results in decrease in the water uptake capacity. This can be due to saturation of water molecules in the polymer matrix, which prevent the water absorption (Xin *et al.* 2014). Studies on SPEEK-GO at different ratios also exhibited similar characteristics of reduction in water uptake capacity with increase in the concentration of the nano filler materials (Leong *et al.* 2015; Ben Liew *et al.* 2020).

IEC indicates the number of acid groups present in one gram of the sample. In general, membranes having higher IEC values will show higher proton conductivity. Ion exchange capacity will also follow the same trend exhibited by water absorption capacity. IEC values of the Nafion, pristine SPEEK and synthesized TiO_2 – SPEEK are shown in Table 1. Composite SPEEK membrane with 5% TiO_2 showed the maximum IEC value of 1.71 meq g^{-1} compared to the other concentrations and pristine SPEEK membrane. Both water uptake capacity and ion exchange capacity values of the SPEEK membrane are higher compared to the commercial Nafion membrane. These two properties have a significant effect on the proton conductivity of the membrane. Thickness values of all the membranes were in the range of 118 μm to 122 μm.

3.2. Fourier transform infrared spectroscopy

Functional group analysis and doping efficiency of TiO_2 over the SPEEK surface were analyzed by FT-IR in the wave number ranges from 400 cm^{-1} to 4,000 cm^{-1}. FTIR spectra of SPEEK and TiO_2 – SPEEK composite membranes are shown in Figure 2. SPEEK and TiO_2-doped SPEEK presented several peaks at the fingerprint region between 500 and 1,500 cm^{-1}. The small peak at 1,617.87 cm^{-1} represents the N–H bend of primary amines and the peak was slowly dissipated when the concentration of TiO_2 increased. This represented the participation of primary amine groups in the doping process of TiO_2 with SPEEK. The medium peak at 1,532.3 cm^{-1} and small sharp peak at 1,343 cm^{-1} depicted the presence of N–O asymmetric stretch of nitro compounds. The peak length decreases with the increase in the concentration of TiO_2 from

Table 1 | Properties of the membrane

Parameters	Nafion	SPEEK	2.5% TiO_2 – SPEEK	5% TiO_2 – SPEEK	7.5% TiO_2 – SPEEK	10% TiO_2 – SPEEK
Water uptake capacity (%)	23	26.14	28.59	31.01	30.54	29.98
Ion exchange capacity (meq/g)	1.13	1.5	1.62	1.71	1.68	1.65
Thickness (μm)	120	121	118	119	122	119

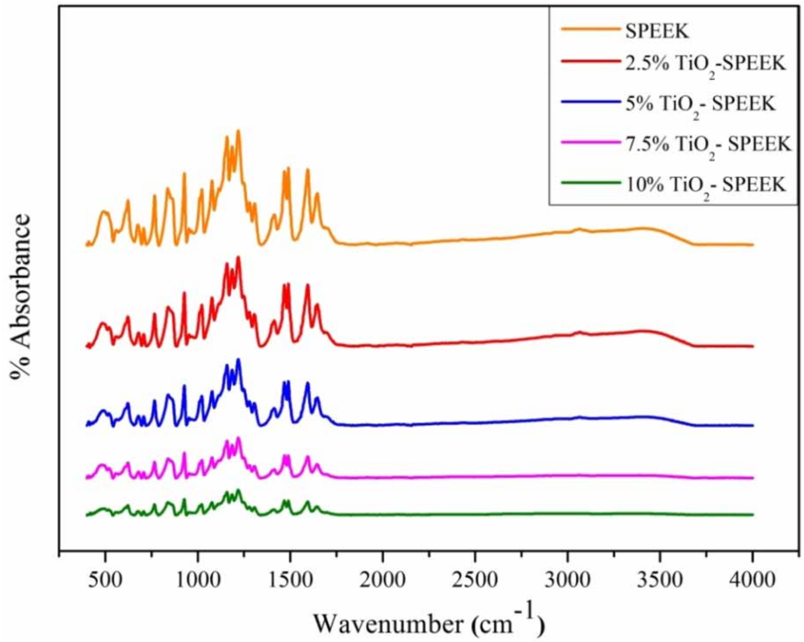

Figure 2 | FT-IR spectra of SPEEK and TiO_2 – SPEEK composite membranes.

2.5% to 10%. This depicted that 10% TiO_2 bound firmly over the SPEEK functional groups through N–O asymmetric stretch of nitro compounds. 1,093 cm^{-1} revealed the existence of C–O stretch alcohols or carboxylic acids of SPEEK.

Disappearance of the sharpness of the peaks for 7.5 and 10% TiO_2-doped SPEEK elucidated that carboxyl groups of alcohols or carboxylic acids took part in the doping of TiO_2 intensively rather than the other concentrations of TiO_2 where the peaks have slight variations at the same wave number. Small peak at 887 cm^{-1} represent the C–H group of aromatics. Variation of the peaks in TiO_2-doped SPEEK clearly represented the involvement of aromatic groups of SPEEK. Slightly broad peak at 724 cm^{-1} showed the existence of C–H group of alkanes and disappearance of the peak at 10% TiO_2 doped SPEEK revealed the participation of alkane groups during the doping process. The peaks remained unchanged for the lower concentrations of doped SPEEK and showed that a minimum of 10% concentration is needed to accomplish strong doping of TiO_2 onto SPEEK with interactive functional groups.

3.3. X-ray diffraction

XRD patterns of SPEEK and TiO_2 – SPEEK composite membranes are shown in Figure 3. All the membranes exhibited a broad diffractive peak at 2 theta angle of about 20°. This shows the semi crystalline nature of the SPEEK membrane. Addition of nano fillers exhibited a decrease in the intensity of the peak at 2 theta angle of about 20°, which denotes the change in crystalline nature to amorphous structure. The change in crystalline nature is observed while the nano filler concentration is increased step by step up to 10%. This result confirms the amorphous nature of the membrane.

3.4. Raman spectroscopy

The Figure 4 shows the Raman spectra of SPEEK and TiO_2 compositions with increasing concentration from 2.5% to 10%. The Raman weak vibration modes at 285, 458, and 680 cm^{-1} attribute the presence of the carbon backbone of SPEEK polymer and Ti bonds. The appearance of a high intensity band at 1,100 and 1,650 cm^{-1} is mainly due to the presence of the ketonic (C=O) bond and C-O-C linkage of the sulfonated poly(ether ether ketone) which could be seen in all the spectra. The Ti-O-H symmetrical stretching can be observed at 925 cm^{-1}. The clear appearance of strong band at 634 cm^{-1} confirms the presence of the rutile phase of TiO_2, which is due to the Eg vibrating mode of the anatase phase. It is also evident that the additional Ti-O bonded with the sulfonic acid group of the SPEEK network. As we can see that increasing the concentration from 2.5 to 10% of TiO_2 decreases the intensity of the Raman mode at 1,650 cm^{-1} that corresponds to the C-O-C back bone of the SPEEK. The observation clearly suggests that formation of the additional bonding of O-Ti-O bonding with O-C-O network.

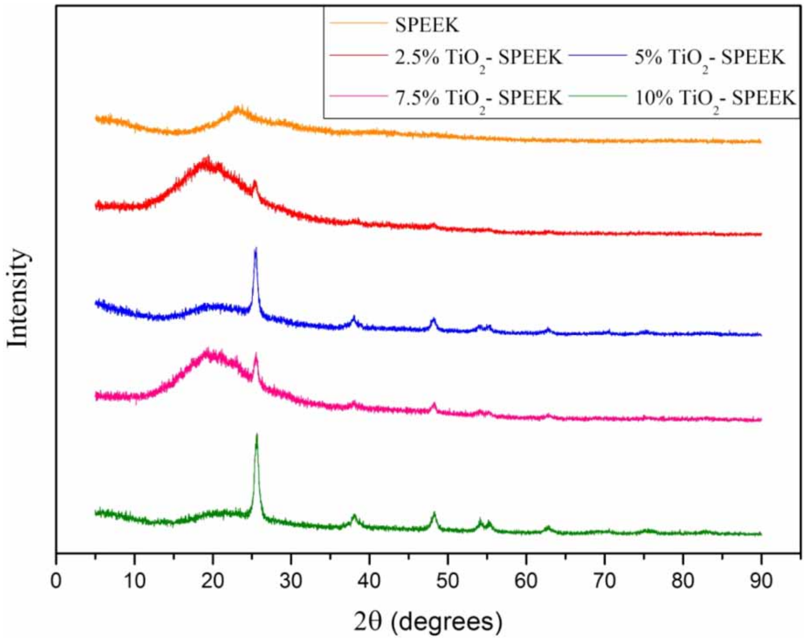

Figure 3 | XRD spectra of SPEEK and TiO_2 – SPEEK composite membranes.

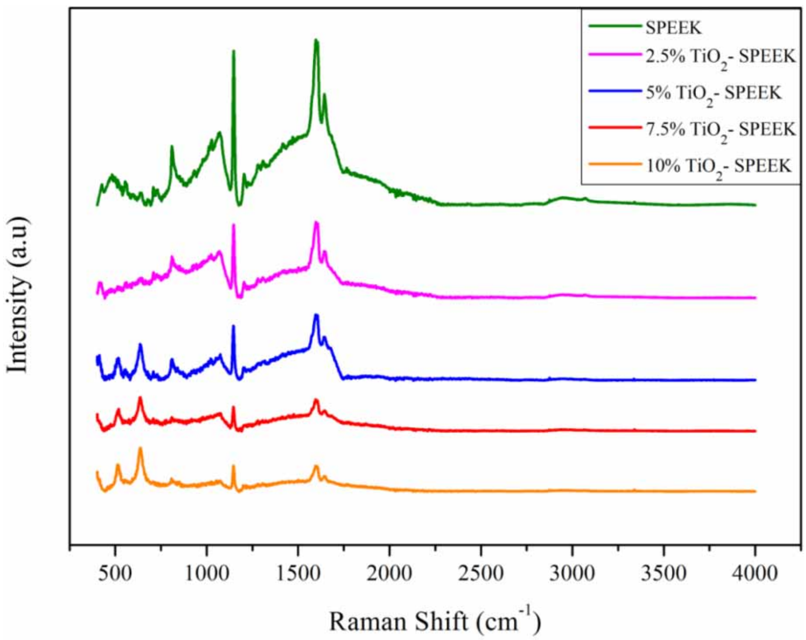

Figure 4 | Raman spectra of SPEEK and TiO_2 – SPEEK composite membranes.

3.5. Scanning electron microscopy

SEM images of the SPEEK and TiO_2 – SPEEK composite membranes with varying weight percentages are shown in Figure 5. The surface morphology of SPEEK membrane was found to be very smooth and uniform without any porous structure. Images of the composite membranes also exhibited a similar morphology with uniform surface without any pores up to 5%. This shows that nanofiller TiO_2 has been dispersed uniformly over the SPEEK polymer matrix. Few agglomerations of TiO_2 were observed at higher weight percentage of 7.5 and 10%.

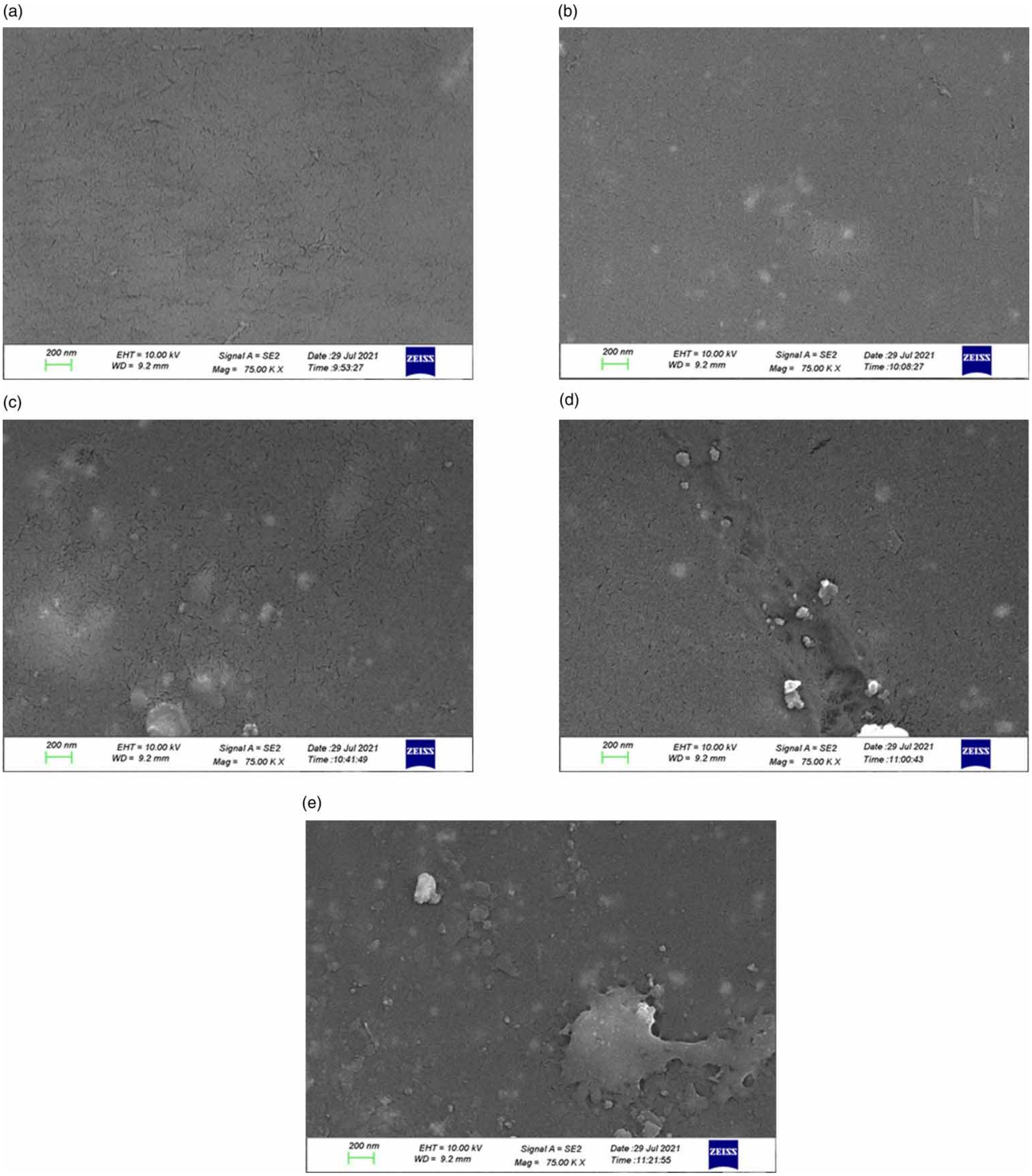

Figure 5 | SEM images of SPEEK and composite membranes (a) SPEEK, (b) 2.5% TiO_2 – SPEEK, (c) 5% TiO_2 – SPEEK, (d) 7.5% TiO_2 – SPEEK, (e) 10% TiO_2 – SPEEK.

3.6. Thermo gravimetric analysis

Thermal stability of the prepared SPEEK and TiO_2 – SPEEK composite membranes were evaluated using TGA analysis. Variation of percentage weight loss in the membranes with respect to increase in temperature was plotted and depicted in the Figure 6. From the plot it is observed that the membranes degraded in three phases. The first phase of weight loss starts about 100 °C. This weight loss is mostly attributed to the evaporation of water molecules adsorbed over the hydrophilic groups present the polymer matrix. Second phase of weight loss takes place between 100 °C and 400 °C. Weight loss in this phase is attributed to the evaporation of residual solvent such as NMP and the sulfonic groups attached to the polymeric matrix. Third phase of weight loss begins around 450 °C and ends at 650 °C corresponding to the degradation of the polymeric matrix.

3.7. Mechanical stability

Mechanical stability of SPEEK and TiO_2 – SPEEK composite membranes was evaluated by UTM. Young's Modulus (N/mm^2), percentage elongation and tensile strength (N/mm^2) values of the SPEEK and SPEEK composite membranes are presented in Table 2. Results show that the mechanical stability of the SPEEK membrane can be improved by the addition of TiO_2 nano particles.

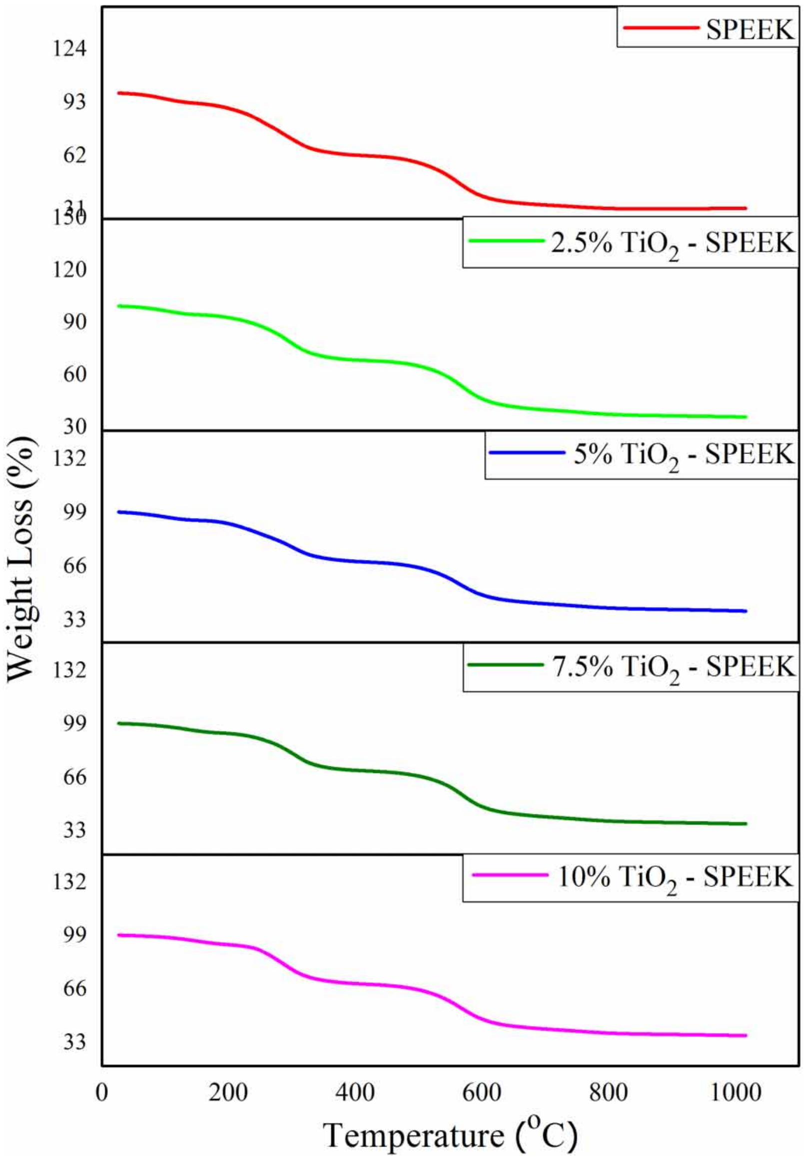

Figure 6 | Thermo Gravimetric Analysis of SPEEK and TiO_2 – SPEEK composite membranes.

Table 2 | Mechanical properties of SPEEK and TiO_2 – SPEEK composite membranes

Membrane	%Elongation	Young's Modulus N/mm^2	Tensile strength N/mm^2
SPEEK	2.28247	9.69940	22.1385
2.5% TiO_2 – SPEEK	3.17972	8.79599	27.9687
5% TiO_2 – SPEEK	3.53808	8.27500	29.2776
7.5% TiO_2 – SPEEK	2.47972	8.39360	20.8137
10% TiO_2 – SPEEK	1.57692	8.11145	12.7911

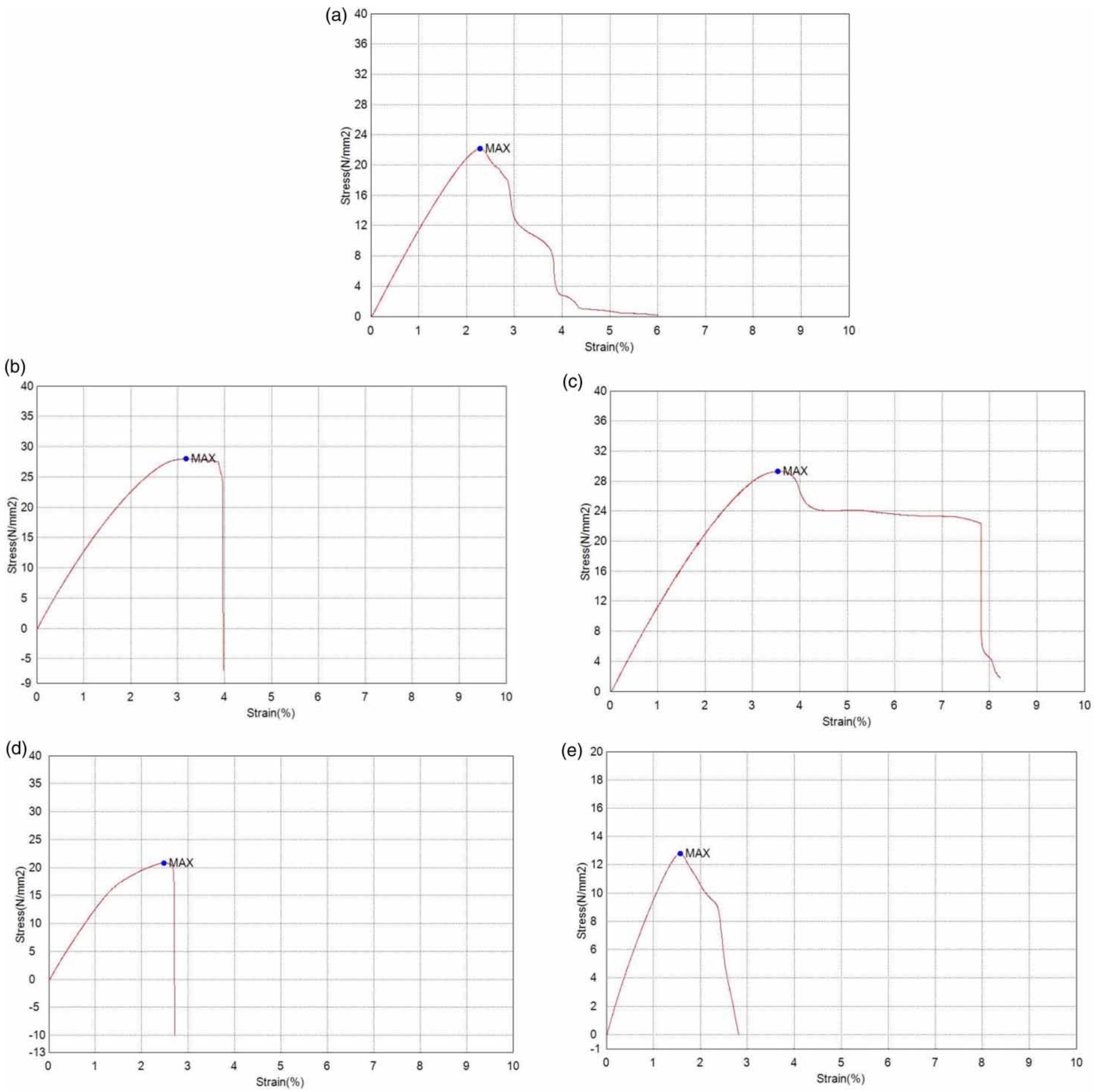

Figure 7 | Stress-strain curves of SPEEK and composite membranes (a) SPEEK, (b) 2.5% TiO_2 – SPEEK, (c) 5% TiO_2 – SPEEK, (d) 7.5% TiO_2 – SPEEK, (e) 10% TiO_2 – SPEEK.

Increase in the tensile strength of the SPEEK composite is ascribed to the nano fillers, which act as a reinforcing agent to support the polymeric matrix. Tensile strength of the SPEEK membrane increased from 22.14 N/mm^2 to 29.28 N/mm^2 with addition of 5% TiO_2. Further increase in the TiO_2 weight percentage to 7.5 and 10% exhibited a decrease in the tensile strength value from 29.28 N/mm^2 to 20.82 and 12.79 N/mm^2 respectively. Reason for the decrease in the tensile at higher TiO_2 weight percentage is attributed to the aggregation of the TiO_2 nano particles over the SPEEK polymer matrix. Stress-strain curves for the SPEEK and SPEEK composite membranes are presented in Figure 7. From this curve it is seen that 5% TiO_2 – SPEEK composite membrane alone exhibited a greater yielding and also has a higher strain value compared to other membranes.

3.8. Electrochemical characterization of SPEEK composite membranes

The CV plots for the MFC system with TiO_2 – SPEEK composite membranes are shown in Figure 8. CV studies were conducted for unmodified SPEEK membrane and TiO_2 modified SPEEK membranes. Unmodified SPEEK membrane is showing a high oxidation peak current at −0.9 V. After modified with TiO_2 the membrane showed a high intensity oxidation and reduction peaks. Of these modified membranes 5% TiO_2 modified SPEEK membrane exhibited the highest oxidation current value at −0.3 V and reduction peak at 0.2 V. It is inferred that modified SPEEK membranes are electrochemically active compared to unmodified SPEEK membrane.

3.9. Power generation in MFC operation

Synthesized composite SPEEK membrane with varying TiO_2 concentrations were tested in the fabricated dual chambered microbial fuel cell system. The closed circuit voltage (CCV) and power density of MFCs with SPEEK membrane and composite SPEEK membrane with 2.5%, 5%, 7.5% & 10% TiO_2 are measured and depicted in Figure 9 and 10 respectively. From the figure it is understood that SPEEK with 5% TiO_2 produced the maximum CCV of 0.64 V and maximum power density of 1.22 W/m^2 on the fifth day. Obtained CCV values for the MFCs with different membranes also followed a similar trend seen in the membrane properties values. This trend in power values is due to membrane properties (water uptake, proton conductivity and ion exchange capacity) which are directly related to power generation. Apart from membrane characteristics, other parameters such electrodes, bio film growth also play a vital role in the power generation. Power density values for the obtained closed circuit voltage were calculated using the formula mentioned in the calculations. The calculated power density and current density values for the MFC with different membranes were tabulated in Table 3. The power density

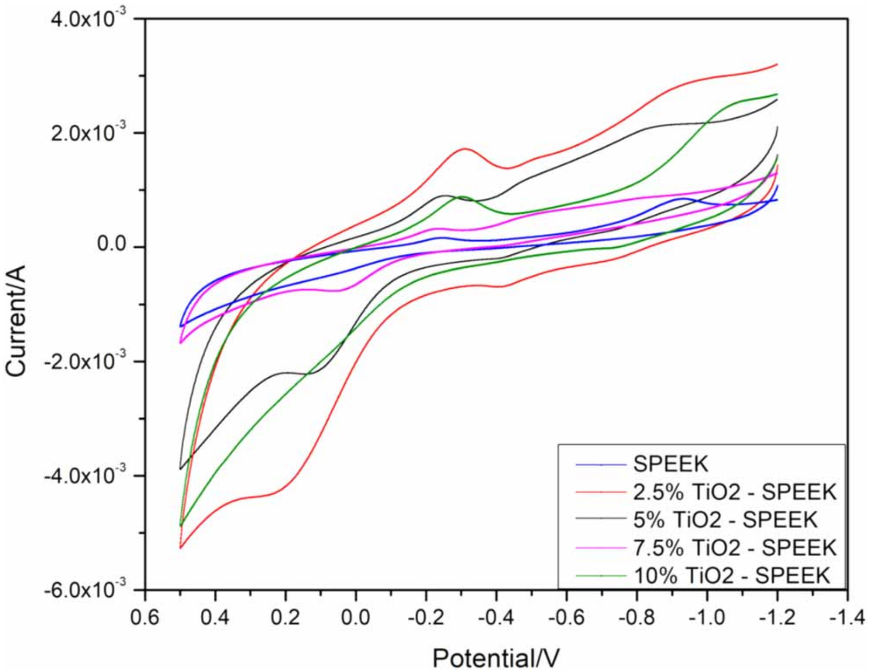

Figure 8 | CV plots for MFCs with SPEEK composite membranes.

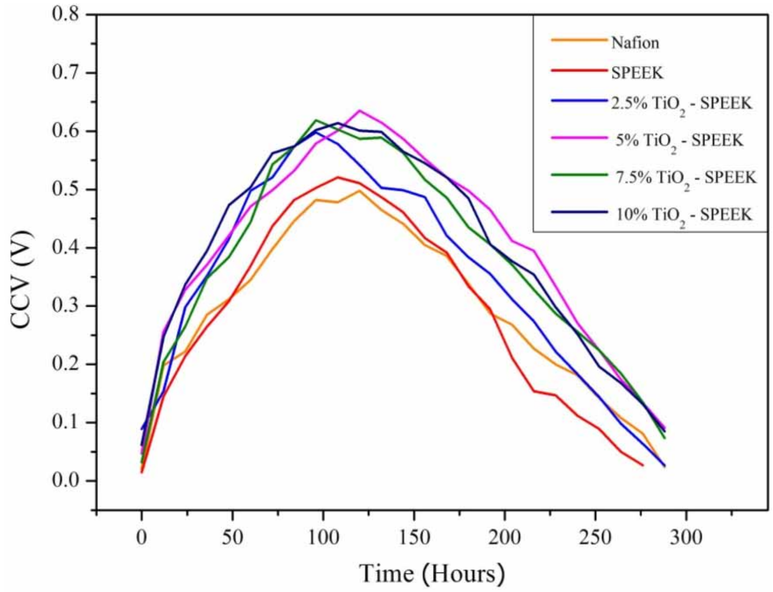

Figure 9 | CCV of MFC with Nafion, SPEEK and TiO_2 – SPEEK composite membranes.

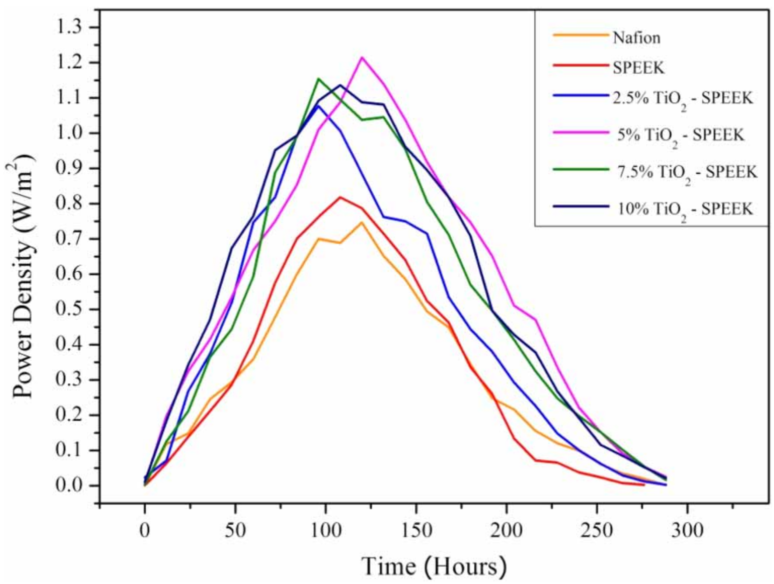

Figure 10 | Power density of MFC with Nafion, SPEEK and TiO_2 – SPEEK composite membranes.

Table 3 | MFC performances with of SPEEK and TiO_2 – SPEEK composite membranes

Parameters	Nafion	SPEEK	2.5% TiO_2 – SPEEK	5% TiO_2 – SPEEK	7.5% TiO_2 – SPEEK	10% TiO_2 – SPEEK
Maximum CCV (V)	0.498 at the 120th hour	0.521 at the 108th hour	0.598 at the 96th hour	0.635 at the 120th hour	0.619 at the 96th hour	0.614 at the 108th hour
Maximum power density (W/m^2)	0.75	0.82	1.08	1.22	1.15	1.14

values obtained in the study is found comparable to the results reported in the study carried out using SPEEK- TiO_2-SO_3H composite membrane (1.20 W/m^2) in single chambered microbial fuel cell (Ayyaru & Dharmalingam 2015).

3.10. Wastewater treatment efficiency

MFCs with different membranes were also evaluated for their wastewater treatment efficiency. Different parameters such as COD, BOD, TOC and turbidity of synthetic dairy wastewater were analyzed prior to the usage in the MFC system. After testing the MFC with different membranes used in the study, characteristics of the wastewater was finally analyzed. Results of the various parameters considered in the study are shown in Table 4. From the results it is found that COD removal efficiency is around 90%. Nafion membrane exhibited higher COD removal efficiency compared to the other membranes considered. Similarly, results of the BOD removal efficiency, TOC reduction and turbidity reduction were also found to be in the range of 90%.

3.11. Evaluation of biofilm growth

The biofilm formation on anode materials is one of the essential factors to be considered in the MFC operation. Electron transfer mechanism and the biodegradability of the organic matters in the substrate are directly related to the biofilm

Table 4 | Wastewater treatment efficiency

Characteristics		Nafion	SPEEK	2.5% TiO_2 – SPEEK	5% TiO_2 – SPEEK	7.5% TiO_2 – SPEEK	10% TiO_2 – SPEEK
COD (mg/l)	Initial	2,418	2,418	2,418	2,418	2,418	2,418
	Final	215	275	218	249	309	298
	% Removal	91.11	88.63	90.98	89.70	87.22	87.68
BOD (mg/l)	Initial	1,185	1,185	1,185	1,185	1,185	1,185
	Final	166	214	190	143	202	172
	% Removal	85.99	81.94	83.97	87.93	82.95	85.49
TOC (ppm)	Initial	724	724	724	724	724	724
	Final	65	72	57	79	87	70
	% Removal	91.02	90.06	92.13	89.09	87.98	90.33
Turbidity (NTU)	Initial	409	409	409	409	409	409
	Final	45	54	41	53	58	64
	% Removal	89.00	86.80	89.98	87.04	85.82	84.35

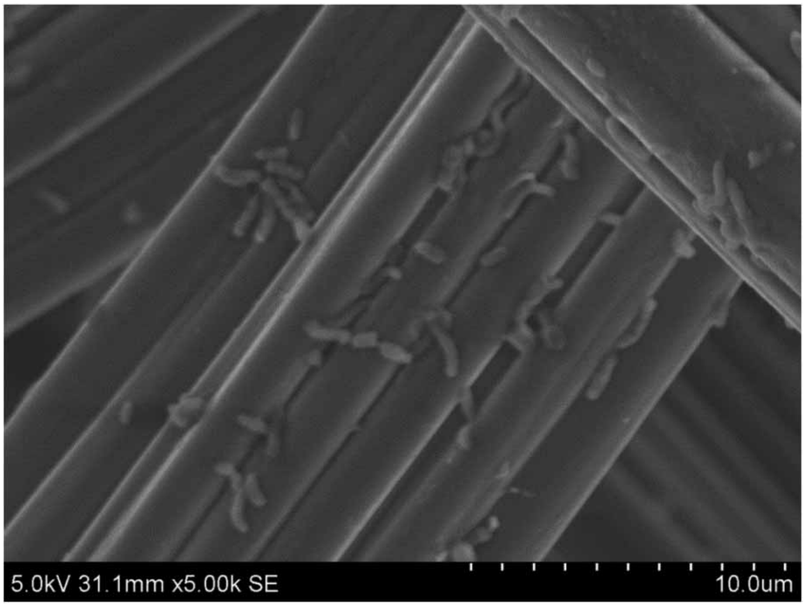

Figure 11 | Biofilm growth on the surface of the electrode used in the MFC system.

formation on the anode material. Hence, it is mandatory to check the biofilm growth on the surface of the material. This can be carried out using the SEM analysis of the electrodes after performing the experiments. An SEM image of the carbon cloth used in the 5% TiO_2 – SPEEK membrane setup is shown in Figure 11. The image confirms the biofilm formation on the surface of the electrodes. The thickness and the concentration of the biofilm formation depend on the significant organic sources present in the wastewater. It also depends on the surface properties of the anode material for adhesion of microbes. All the three electrodes were found to have good biofilm formation, which was reflected in the COD reduction in the treated wastewater. The different shapes (rod and oval) of microorganisms reveal the presence of various types of microbes in the anodic biofilm.

4. CONCLUSION

In this study, SPEEK and composite SPEEK membrane incorporated with varying concentrations of TiO_2 nano materials were successfully synthesized, characterized and tested in an MFC system. Varying the TiO_2 concentration in a SPEEK composite membrane showed a significant effect on the membrane characteristics and its performance in the MFC system. FT-IR spectra for SPEEK composite membrane reveal the dispersion of the TiO_2 fillers into the SPEEK matrix and it is confirmed by XRD patterns with the transformation of the semi-crystalline structure to an amorphous structure. Composite membranes also exhibited a better stability against thermal and mechanical load. Composite SPEEK membrane exhibited better values for water uptake capacity and ion exchange capacity in comparison to the pristine SPEEK and commercial Nafion membrane. From the results it was found that 5% TiO_2 – SPEEK membrane showed good performance in terms of membrane characteristics and power generation. COD removal efficiency of all composite SPEEK membranes was found to be in the range of 90%. Results from this study prove that composite SPEEK membrane has the potential to replace the high-cost Nafion membrane in MFC systems.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Asha, B. & Elakkiya, S. 2014 Feasibility studies on the treatment of synthetic dairy wastewater under variable experimental conditions. *Nature Environment and Pollution Technology* **13** (4), 851.

Ayyaru, S. & Dharmalingam, S. 2013 Improved performance of microbial fuel cells using sulfonated polyether ether ketone (SPEEK) TiO_2-SO_3H nanocomposite membrane. *RSC Advances* **3** (47), 25243–25251. https://doi.org/10.1039/c3ra44212 h.

Ayyaru, S. & Dharmalingam, S. 2015 A study of influence on nanocomposite membrane of sulfonated TiO_2 and sulfonated polystyrene-ethylene-butylene-polystyrene for microbial fuel cell application. *Energy* **88**, 202–208. https://doi.org/10.1016/j.energy.2015.05.015.

Ben Liew, K., Leong, J. X., Wan Daud, W. R., Ahmad, A., Hwang, J. J. & Wu, W. 2020 Incorporation of silver graphene oxide and graphene oxide nanoparticles in sulfonated polyether ether ketone membrane for power generation in microbial fuel cell. *Journal of Power Sources* **449** (April), 227490. https://doi.org/10.1016/j.jpowsour.2019.227490.

Dou, Z., Zhong, S., Zhao, C., Li, X., Fu, T. & Na, H. 2008 Synthesis and characterization of a series of SPEEK/TiO_2 hybrid membranes for direct methanol fuel cell. *Journal of Applied Polymer Science* **109** (2), 1057–1062. https://doi.org/10.1002/app.25127.

Du, Z., Li, H. & Gu, T. 2007 A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. *Biotechnology Advances* **25** (5), 464–482. https://doi.org/10.1016/j.biotechadv.2007.05.004.

Faria, A., Gonçalves, L., Peixoto, J. M., Peixoto, L., Brito, A. G. & Martins, G. 2017 Resources recovery in the dairy industry: bioelectricity production using a continuous microbial fuel cell. *Journal of Cleaner Production* **140**, 971–976. https://doi.org/10.1016/j.jclepro.2016.04.027.

Fratesi, S. E., Lynch, F. L., Kirkland, B. L. & Brown, L. R. 2004 Effects of SEM preparation techniques on the appearance of bacteria and biofilms in the Carter sandstone. *Journal of Sedimentary Research* **74** (6), 858–867. https://doi.org/10.1306/042604740858.

Gavimath, C. C., Hooli, V. R. & Patil, a. B. 2012 Generation of bioelectricity using waste water. *International Journal of Advanced Biotechnology and Research* **3** (1), 537–540.

Ji, B., Zhao, Y., Vymazal, J., Mander, Ü., Lust, R. & Tang, C. 2021 Mapping the field of constructed wetland-microbial fuel cell: a review and bibliometric analysis. *Chemosphere* **262**, 128366. https://doi.org/10.1016/j.chemosphere.2020.128366.

Kaur, R., Marwaha, A., Chhabra, V. A., Kim, K. H. & Tripathi, S. K. 2020 Recent developments on functional nanomaterial-based electrodes for microbial fuel cells. *Renewable and Sustainable Energy Reviews* **119** (July), 109551. https://doi.org/10.1016/j.rser.2019.109551.

Leong, J. X., Daud, W. R. W., Ghasemi, M., Ahmad, A., Ismail, M. & Liew, K. B. 2015 Composite membrane containing graphene oxide in sulfonated polyether ether ketone in microbial fuel cell applications. *International Journal of Hydrogen Energy* **40** (35), 11604–11614. https://doi.org/10.1016/j.ijhydene.2015.04.082.

Logan, B. E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. & Rabaey, K. 2006 Microbial fuel cells: methodology and technology. *Environmental Science and Technology* **40** (17), 5181–5192. https://doi.org/10.1021/es0605016.

Mohtar, S. S., Ismail, A. F. & Matsuura, T. 2011 Preparation and characterization of SPEEK/MMT-STA composite membrane for DMFC application. *Journal of Membrane Science* **371** (1–2), 10–19.

Nam, T., Son, S., Koo, B., Hoa Tran, H. V., Kim, J. R., Choi, Y. & Jung, S. P. 2017 Comparative evaluation of performance and electrochemistry of microbial fuel cells with different anode structures and materials. *International Journal of Hydrogen Energy* **42** (45), 27677–27684. https://doi.org/10.1016/j.ijhydene.2017.07.180.

Nimje, V. R., Chen, C. Y., Chen, H. R., Chen, C. C., Huang, Y. M., Tseng, M. J., Cheng, K. C. & Chang, Y. F. 2012 Comparative bioelectricity production from various wastewaters in microbial fuel cells using mixed cultures and a pure strain of *Shewanella oneidensis*. *Bioresource Technology* **104**, 315–323. https://doi.org/10.1016/j.biortech.2011.09.129.

Patra, A. 2008 Low-cost, single-chambered microbial fuel cells for harvesting energy and cleansing wastewater. *Journal of the US, SJWP*. 72–85. Available from: http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Low-Cost+,+Single-Chambered+Microbial+Fuel+Cells+for+Harvesting+Energy+and+Cleansing+Wastewater#0

Peeva, G., Yemendzhiev, H., Bonev, B., Zerrouq, F. & Nenov, V. 2014 Anaerobic organic matter degradation in microbial fuel cell. *Journal of Materials and Environmental Science* **5** (July 2015), 2350–2353.

Santoro, C., Arbizzani, C., Erable, B. & Ieropoulos, I. 2017 Microbial fuel cells: from fundamentals to applications. A review. *Journal of Power Sources* **356**, 225–244. https://doi.org/10.1016/j.jpowsour.2017.03.109.

Singh, D., Pratap, D., Baranwal, Y., Kumar, B. & Chaudhary, R. K. 2010 Microbial fuel cells: a Green technology for power generation. *Annals of Biological Research* **1** (3), 128–138. Available from: http://scholarsresearchlibrary.com/archive.html.

Tiwari, T., Kumar, M., Yadav, M. & Srivastava, N. 2019 Study of arrowroot starch-based polymer electrolytes and its application in MFC. *Starch/Staerke* **71** (7–8), 1–8. https://doi.org/10.1002/star.201800313.

Vidhyeswari, D. & Bhuvaneshwari, S. 2018 Treatment of dairy wastewater and performance comparison of three different electrodes in microbial fuel cell system. *Desalination and Water Treatment* **122**, 323–330. https://doi.org/10.5004/dwt.2018.22969.

Xin, Q., Wu, H., Jiang, Z., Li, Y., Wang, S., Li, Q., Li, X., Lu, X., Cao, X. & Yang, J. 2014 SPEEK/amine-functionalized TiO_2 submicrospheres mixed matrix membranes for CO_2 separation. *Journal of Membrane Science* **467**, 23–35. https://doi.org/10.1016/j.memsci.2014.04.048.

Yazdi, A. A., D'Angelo, L., Omer, N., Windiasti, G., Lu, X. & Xu, J. 2016 Carbon nanotube modification of microbial fuel cell electrodes. *Biosensors and Bioelectronics* **85**, 536–552. https://doi.org/10.1016/j.bios.2016.05.033.

First received 30 June 2021; accepted in revised form 8 October 2021. Available online 27 October 2021