Research Article

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TiO_2-doped sulfonated poly(etheretherketone)/poly(vinyl alcohol) blend membrane synthesis for microbial fuel cell systems

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Abstract

This study explores the development and comprehensive evaluation of titanium dioxide (TiO_2)-doped, thermally crosslinked sulfonated poly(ether ether ketone) (SPEEK)/poly(vinyl alcohol) (PVA) blend membranes for microbial fuel cell (MFC) applications. The membranes were synthesized with varying TiO_2 concentrations and characterized through analyses of water content, ion exchange capacity, swelling behavior, mechanical strength, electrochemical impedance spectroscopy and Fourier transform infrared spectroscopy. Incorporation of TiO_2 significantly enhanced proton conductivity and reduced water-induced mass loss compared to undoped membranes. Among the various compositions, the membrane containing 5 wt% TiO_2 (SPEEK/PVA-5T) demonstrated the highest proton conductivity of 0.4346 S cm^{-1} at 25 °C, indicating superior performance. The membranes were tested in a cylindrical H-type MFC setup. The SPEEK/PVA-5T membrane achieved a maximum voltage output of 560.610 mV and a power density of 62.856 μW m^{-2}, in comparison to a commercial Nafion 117 membrane, which delivered 777.740 mV and 120.975 μW m^{-2}. These findings underscore the potential of the SPEEK/PVA-5T membrane as an effective and sustainable alternative for MFC applications, offering enhanced ion transport and contributing to the advancement of carbon-neutral energy technologies. This work represents a meaningful step toward the development of high-performance, eco-friendly membrane materials for renewable energy systems.

Keywords: membrane synthesis; TiO_2-doped membrane; Nafion 117 membrane; microbial fuel cell

INTRODUCTION

Energy has long been a fundamental driver of human development across the globe. However, conventional energy sources such as coal, oil and natural gas are major contributors to environmental pollution.[1] The resulting environmental degradation and energy-related challenges pose significant threats to both ecosystems and human health.[2] Therefore, the development of renewable energy sources is essential to mitigate environmental pollution and support sustainable economic growth.[3] Renewable energy options include wind, tidal, geothermal, solar, biomass, hydroelectric power and fuel cell technologies.[4] Among these, microbial fuel cells (MFCs) represent a promising type of fuel cell that harnesses the catalytic activity of microorganisms to generate electricity.[5] MFCs are bioelectrochemical systems that utilize microorganisms to catalyze the oxidation of organic or inorganic matter, producing electrical energy in the process.[6] These systems are environmentally friendly and enable the conversion of biodegradable substrates into usable power.[7]

Unlike conventional wastewater treatment methods, MFCs offer the unique advantage of simultaneous wastewater treatment and electricity generation.[8] A typical MFC consists of an anode and a cathode, separated by a proton exchange membrane, and connected through an external circuit to facilitate current flow.[9]

Simultaneously, protons are generated in the anode chamber through the proton exchange membrane to the cathode chamber.[10] Generally, an MFC can be separated by a proton exchange membrane such as Nafion. Nafion has disadvantages, such as oxygen leakage from the cathode to the anode, substrate loss, biofouling, inability to cope at high temperature and high cost.[11–13] Hence, researchers have focused on developing an economic membrane that can be an alternative to Nafion commercial membranes. Nafion-modified membrane studies are generally focused on the composite structure formed by the Nafion membrane with an inorganic filling material or a polymer.[11,14–20] In the last few

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years, poly(ether ether ketone) (PEEK) has been widely studied as a polymer membrane material in MFC systems.[21–25]

Sulfonated PEEK (SPEEK) with an optimized degree of sulfonation (DS) could give promising results compared to Nafion commercial membranes.[26,27] SPEEK was synthesized by keeping the DS in the 47–77% range. It was observed that increasing the DS disrupts the structural integrity of the membrane. A blend membrane containing 4 wt% SPEEK with a 47% DS indicated the best results. In another study, a titanium dioxide (TiO_2)-doped SPEEK composite membrane was synthesized, and the SPEEK DS was determined as 50% and 63%.[28] In another study, tungstophosphoric acid caesium salt-doped SPEEK composite membrane was synthesized at DSs of 60%, 70% and 82%.[29] The results indicated that the SPEEK with a 40% DS had higher thermal and mechanical stability than Nafion 117. In recent years, SPEEK-based membrane studies have mainly focused on wastewater treatment for MFC systems.[23,30–37] Additive materials were used as composite materials, such as silicon dioxide (SiO_2)[38] and TiO_2.[39]

The aim of the study presented here was to develop a novel membrane with a chemical composition distinct from those used in previous MFC studies involving separate anode and cathode chambers. Based on the findings, it is anticipated that the improved membrane design could enhance the performance of MFCs, enabling not only laboratory-scale applications but also potential large-scale implementations. Compared to conventional wastewater treatment systems, MFCs offer substantial advantages by simultaneously reducing waste and generating energy, leading to significant cost and energy savings.

EXPERIMENTAL

The sulfonation of PEEK and the synthesis of both SPEEK/poly (vinyl alcohol) (PVA) and TiO_2-doped SPEEK/PVA membranes were performed. The synthesized membranes were characterized using various procedures.

Materials

In this study, PEEK (99% w/w, M_w: 20 800 g mol^{-1}) was employed as the primary polymer of the blend membrane and PVA (99% w/w, M_w: 124 000 g mol^{-1}) was used as a second polymer which was purchased from Sigma-Aldrich. Dimethylsulfoxide (DMSO; 99% w/w solution purchased from Sigma-Aldrich) was used as a solvent. Sulfuric acid (H_2SO_4; 99.8% w/w) was bought from Sigma-Aldrich and used as an active group source to sulfonate the PEEK membrane. TiO_2 was purchased from Akerman Group, Ankara, Turkey.

Sulfonation of PEEK

PEEK was dissolved in a preheated H_2SO_4 (1/20 w/v) solution with magnetic stirrer for 6 h at 60 °C. At the end of the specified time, an ice bath was used to halt the reactivity of the black viscous solution. Then, the surplus acid was eliminated by washing and filtering the sulfonated solid polymer. Finally, the neutralized polymer was dried for 12 h at 40 °C in a fan oven.

Blend and doped membrane preparation

DMSO (20:1 v/w) was used as the solvent for the preparation of the SPEEK/PVA blend (90:10 by mass) and TiO_2-doped SPEEK/PVA membranes with varying TiO_2 mass ratios (1, 5 and 7 wt%). Initially, dried SPEEK polymer was added to a preheated DMSO solution and blended at 60 °C for 1 h. Subsequently, a preheated 5 wt% PVA/DMSO solution was added, and the mixture was blended for 48 h at 60 °C. The homogeneous blend was then cast onto a glass plate and dried at 50 °C in a fan oven for 24 h. For the synthesis of TiO_2-doped membranes, the specified amounts of TiO_2 were dissolved in preheated DMSO at 60 °C for 48 h. The resulting solution was mixed using an ultrasonic mixer for 1 h and incorporated into the SPEEK/PVA blend membrane solution. The solution was further blended for 24 h at 60 °C. The obtained uniform composition was cast onto a glass plate and dried at 50 °C in a fan oven for 24 h. The nomenclature and contents of the synthesized membranes are detailed in Table 1.

Thermal crosslinking of the blend membranes

Thermal crosslinking was employed to enhance the water resistance of both SPEEK/PVA blend membranes and TiO_2-doped SPEEK/PVA membranes. For this process, the membranes were placed between glass plates to ensure uniform crosslinking and subjected to controlled thermal treatment in an incubator at 180 °C for 48 h, optimizing crosslinking efficiency.

Characterization and analytical methods

Proton conductivity measurements were performed using a PalmSense4 device in conjunction with a measuring cell, employing the three-probe technique. The experiments were conducted under controlled conditions at 25 °C and 100% relative humidity. The proton conductivity was calculated by Eqn (1):

$$\sigma = \frac{0.425\ \mathrm{cm}}{L \times R \times W} \tag{1}$$

where σ is the estimated proton conductivity; 0.425 cm is the distance between the electrodes; L is the thickness of the membrane; R is the resistance of the membrane; and W is the width of the membrane.[40]

The ion exchange capacity (IEC) of the membranes was experimentally determined using the basic titration method. Membranes were immersed in 2 mol L^{-1} NaCl solution at room temperature for 48 h to exchange protons with sodium ions. Subsequently, the solution was titrated with 0.01 mol L^{-1} NaOH to quantify the exchanged ions. The IEC was calculated using Eqn (2):

$$\mathrm{IEC} = \frac{V_{\mathrm{NaOH}} \times M_{\mathrm{NaOH}}}{W_{\mathrm{dry}}} \tag{2}$$

where the volume of NaOH consumed is V_{NaOH}; the molarity is M_{NaOH}; and the dry membrane mass is W_{dry}. The IEC test was repeated four times for each membrane, and the average value was taken.[40]

For the determination of water content (WC), membranes were cut in 1 × 1 cm^2 dimensions and kept in deionized water at room temperature for 24 h. The WC was determined using Eqn (3):

Table 1. Nomenclature and contents of the synthesized membranes

Membrane	SPEEK (% by mass)	PVA (% by mass)	TiO_2 (% by mass)
SPEEK/PVA	90	10	—
SPEEK/PVA-1T	89.1	9.9	1
SPEEK/PVA-5T	85.5	9.5	5
SPEEK/PVA-7T	83.7	9.3	7

$$\mathrm{WC}=\frac{W_{\mathrm{wet}}-W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \qquad (3)$$

where W_{wet} and W_{dry} represent the dry and wet membrane respective masses. The WC test was repeated four times for each membrane, and the average result was used.

Membranes cut in 1 × 1 cm^2 dimensions were kept at room temperature in deionized water for 24 h to determine the swelling ratio. The swelling ratio was determined using Eqn (4):

$$\text{Swelling ratio}=\frac{L_{\mathrm{wet}}-L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \qquad (4)$$

where L_{wet} is the wet membrane thickness and L_{dry} is the dry membrane thickness. The swelling ratio test was repeated four times for each membrane, and the average value was taken.[40]

The mechanical strength of the membranes was assessed using a Shimadzu AG-1 5 kN mechanical resistivity testing apparatus. The samples were subjected to a strain rate of 2 mm min^{-1}, and the tensile strength as well as elongation at break values were determined for both undoped and doped membranes.

Fourier transform infrared (FTIR) spectroscopy was conducted on the membranes to identify the active functional groups and to confirm the presence of the additives. Absorbance and wavenumber data were obtained using a Jasco FTIR spectrometer.

Scanning electron microscopy (SEM) analysis of the membranes was performed (before use and after use) to reveal the surface morphology and its behavior inside the MFC.

Setup and operation of MFC

A cylindrical H-type MFC was employed to evaluate the performance of Nafion 117 and the $\mathrm{TiO_2}$-doped SPEEK/PVA membrane that demonstrated the most favorable results in the characterization tests. Graphite-based composite electrodes were synthesized in the laboratory with a 2 × (5 × 5) cm^2 surface area and used as anode/cathode electrodes. The experimental setup is shown in Fig. 1.

Anode and cathode electrodes were connected with a 1 MΩ resistor and power density (P) values were obtained using Eqn (5):

$$P=\frac{IV}{A} \qquad (5)$$

where I is the current, V is the voltage and A is the anode surface area.[41]

RESULTS

Reaction time and optimization of parameters

The sulfonation of PEEK was conducted for three distinct reaction durations: 4, 5 and 6 h. Proton conductivity values of 0.0524 and 0.1734 S cm^{-1} and WC values of 24.55% and 27.08% were obtained for the blend membranes containing PEEK sulfonated for 4 and 5 h, respectively. The DS of SPEEK plays a crucial role, as increased sulfonation enhances the presence of sulfonic acid groups, which attract water molecules and positively charged ions.[32] In a study investigating the influence of DS on membrane characteristics, SPEEK membranes subjected to sulfonation for 6 h at 40 and 60 °C demonstrated WC values of 33.8% and 62.1%, respectively.[42] These findings are consistent with the conclusion that increasing the DS of SPEEK enhances the concentration of hydrophilic sulfonic acid groups within the membrane structure, thereby significantly improving its WC. In addition to 90 wt% SPEEK/10 wt% PVA, two more compositions were also synthesized: 85 wt% SPEEK/15 wt% PVA and 80 wt% SPEEK/20 wt% PVA. As the PVA content increased, the weight loss in water correspondingly rose to 6.92% and 8.97%, respectively, which can be attributed to the open hydroxyl ends of PVA molecules that readily form bonds with water, thereby enhancing the membrane's tendency for mass loss in water. Due to the apparent difference in weight loss in water, 90 wt% SPEEK/10 wt% PVA was chosen as the appropriate mass composition for the study.

WC, IEC and swelling

WC and swelling behavior are critical characteristics that significantly impact the proton conductivity of membranes.[43] The ionic conductivity of a membrane is predominantly governed by the WC within the polymer structure. Hence, a higher WC directly correlates with enhanced ionic conductivity.[25] Protons are transported via water molecules, and excessive resistance adversely

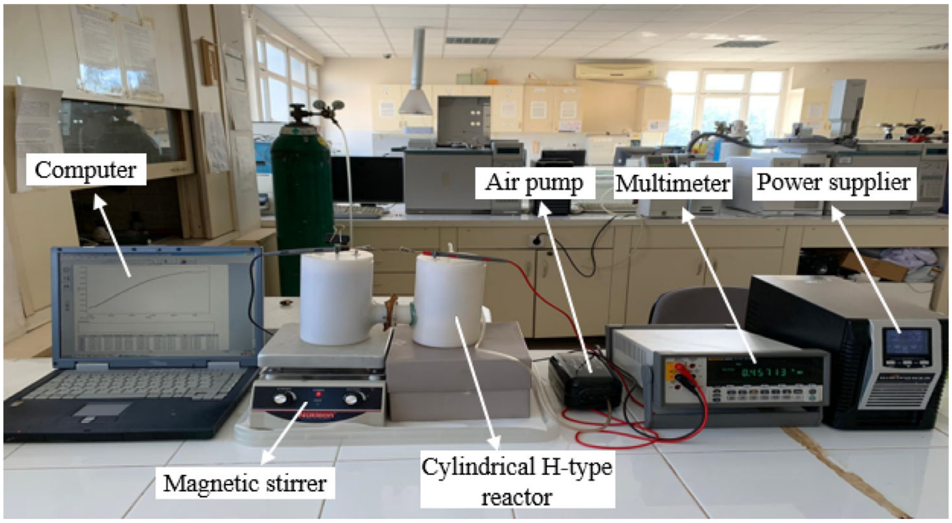

Figure 1. Experimental setup for the performance tests.

affects proton conductivity, thereby compromising membrane performance.[44] In a study where SPEEK membranes were synthesized for proton exchange membrane fuel cells, it was observed that an excessive increase in WC and swelling values led to the loss of mechanical integrity of the membrane.[45] Thus, swelling values should be in alignment with WC values, as excessive swelling is detrimental to achieving optimal membrane performance. Hence, WC, swelling and IEC represent essential characteristics for the comprehensive evaluation of membrane performance. The results for these characteristics of the crosslinked blend membranes, as well as Nafion 117, are presented in Fig. 2.

According to Fig. 2(A), the study has demonstrated that an increase in the WC value of the membrane results in a higher amount of water molecules retained within the membrane, consequently leading to an increase in swelling (Fig. 2(B)) and an enhancement in the IEC value (Fig. 2(C)) due to ionic transfer being facilitated by water molecules. When comparing the swelling values with the swelling ratio per WC to commercial Nafion 117 membrane (31.29%), it is evident that aligning well with the WC values, the ratios are 36.20%, 32.47%, 36.68% and 35.57% for SPEEK/PVA, SPEEK/PVA-1T, SPEEK/PVA-5T and SPEEK/PVA-7T, respectively. Referring to Fig. 2(A),(B), the undoped SPEEK/PVA blend membrane exhibits a WC value of 28.07% and swelling value of 10.16%. In a study where a SPEEK-based proton exchange membrane was synthesized using parameters (50 °C, 5.15 h) similar to those used in this work, the WC value was reported as 23.20% and swelling value of 6.89% at room temperature, yielding comparable results.[44]

The incorporation of TiO_2, known for its hygroscopic nature, significantly enhances the WC values of the membranes.[46,47] As shown in Fig. 2(A), the addition of 1, 5 and 7 wt% TiO_2 into the membrane structure resulted in an increase in WC values from 28.07% to 31.78%, 32.44% and 32.84%, respectively. Since ionic transport within the membrane is facilitated by water molecules, this increase in WC leads to an enhancement in IEC values from 0.14 to 0.15 and 0.16 meq g^{-1}, respectively (Fig. 2(C)). In a study where sulfonated TiO_2 was added to a commercial Nexar membrane, the addition of 3 wt% sulfonated TiO_2 resulted in a 12% increase in the membrane's WC, raising it to 35.6%.[48] Similarly, in another study with results comparable to the present study, the optimal sulfonated TiO_2 content was determined to be 5 wt %, yielding a WC value of 40.9% and a swelling ratio of 11.4%.[49]

Electrochemical impedance spectroscopy

Balancing relative humidity, DS, WC, morphology and chemical composition is essential to optimize the proton conductivity and overall performance of a membrane. Among these, incorporating organic and inorganic additives into the membrane structure significantly improves proton conductivity. In particular, metal oxide-based inorganic additives, such as TiO_2, have demonstrated substantial enhancement in proton conductivity within polymer structures.[21] The proton conductivity results of undoped

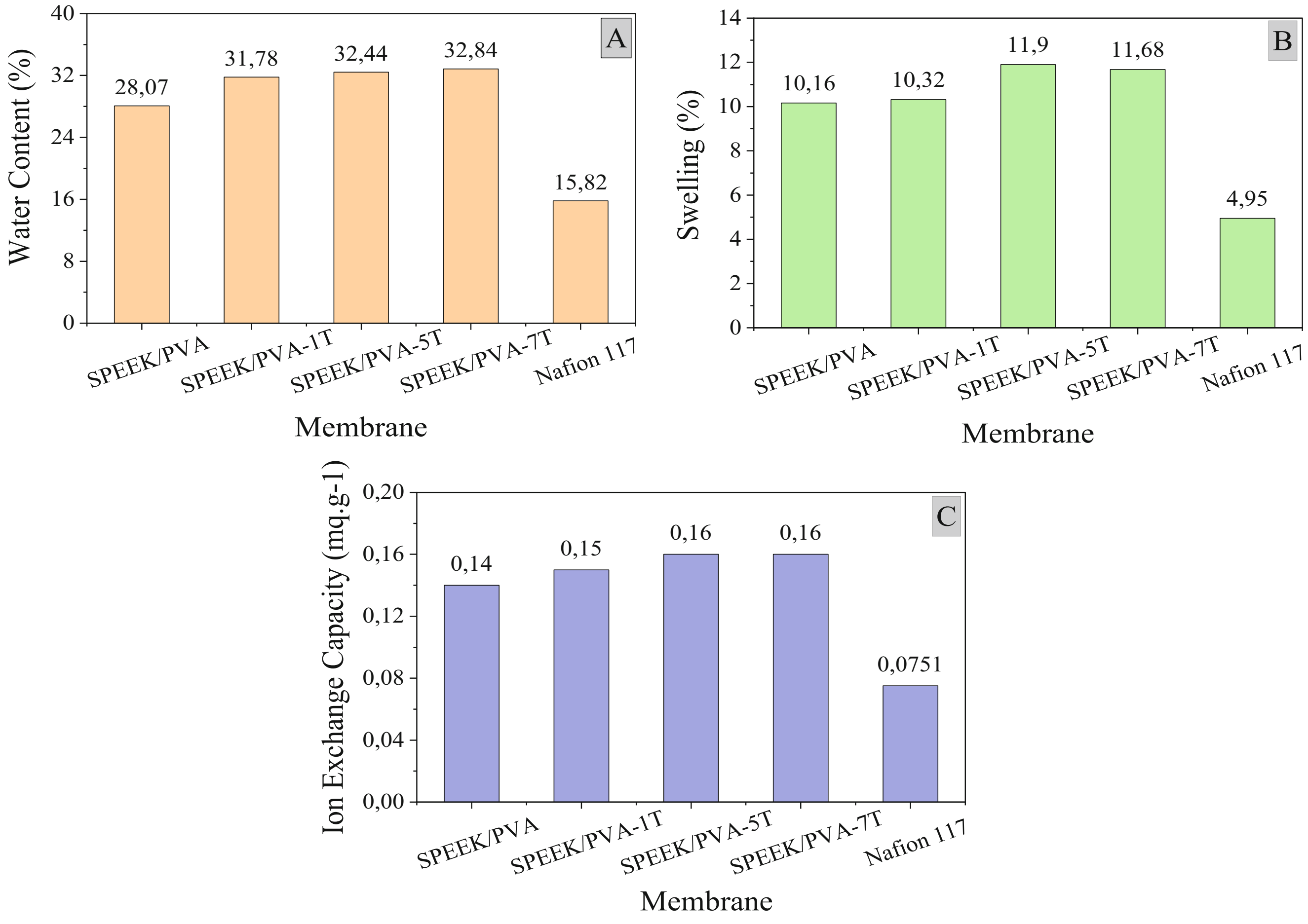

Figure 2. Water content (A), swelling (B) and ion exchange capacity (C) of the blend membranes and Nafion 117.

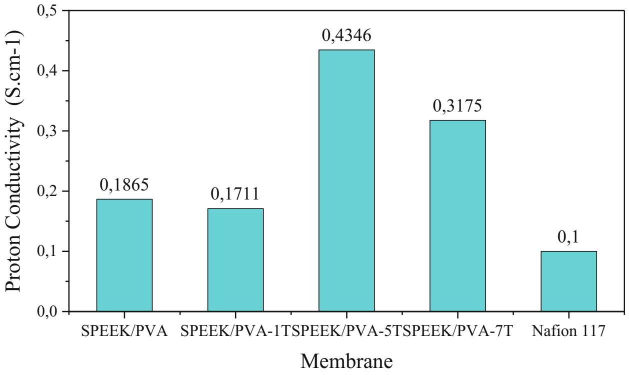

Figure 3. Proton conductivity of TiO_2-doped and undoped blend membranes (at 25 °C and 100% humidity).

Table 2. Mechanical properties of blend membranes and Nafion 117

Membrane	Tensile strength (MPa)	Elongation at break (%)
SPEEK/PVA	34.75	17.08
SPEEK/PVA-1T	25.70	20.83
SPEEK/PVA-5T	47.35	38.58
SPEEK/PVA-7T	23.30	8.29
Nafion 117	13.88	171.82

Table 3. Mass loss of membranes in water at 25 °C

Membrane	Mass loss in water without crosslinking (%)	Mass loss in water with crosslinking (%)
SPEEK/PVA	10.20	3.46
SPEEK/PVA-1T	—	3.05
SPEEK/PVA-5T	—	2.96
SPEEK/PVA-7T	—	2.75
Nafion 117	2.97	—

crosslinked and TiO_2-doped blend membranes at 25 °C and 100% relative humidity are presented in Fig. 3.

According to Fig. 3, the membrane containing 5 wt% TiO_2 exhibited the highest proton conductivity and increased the value from 0.1865 to 0.4346 S cm^{-1}. At this concentration, the additive effectively enhances hydration and proton transport without disrupting the structural integrity of the membrane. In contrast, the addition of 1 wt% TiO_2 did not significantly influence proton conductivity, likely due to the insufficient presence of TiO_2 to create a notable impact on membrane hydration. The membrane with 7 wt% TiO_2 showed lower proton conductivity than the one with 5 wt% due to excess TiO_2 blocking proton pathways. This highlights the importance of optimizing additive content, with 5 wt% TiO_2 being the most effective for SPEEK/PVA membranes.

Similar results were reported in previous studies. TiO_2 addition improved conductivity in various membranes by increasing WC and aiding proton transport.[18,40] In SPEEK membranes for MFCs, 5 wt% TiO_2 enhanced WC (31%) and IEC (1.71 meq g^{-1}), while higher amounts reduced both, likely due to particle agglomeration and blocked pathways.[39]

These findings are consistent with those of the present study, confirming the beneficial role of TiO_2 in proton conductivity, though absolute values vary with membrane type and testing conditions.

Mechanical strength

In MFCs, the mechanical strength of the membrane is critical for ensuring sustained performance and operational stability. Therefore, optimizing mechanical performance is essential for achieving consistent and efficient functionality in MFCs. The mechanical test results of the synthesized blend membranes and the commercial Nafion 117 membrane are presented in Table 2.

It is evident from Table 2 that the addition of TiO_2 also improved the mechanical properties of the membrane. Notably, in another study, the inclusion of TiO_2 in polybenzimidazole membranes was found to significantly enhance their chemical stability and acid retention.[50] The tensile strength of the blend membranes ranges from 23.30 to 47.35 MPa, while their elongation at break varies between 8.29% and 38.58%. Among these, the SPEEK/PVA-5T membrane exhibits the highest tensile strength, reaching

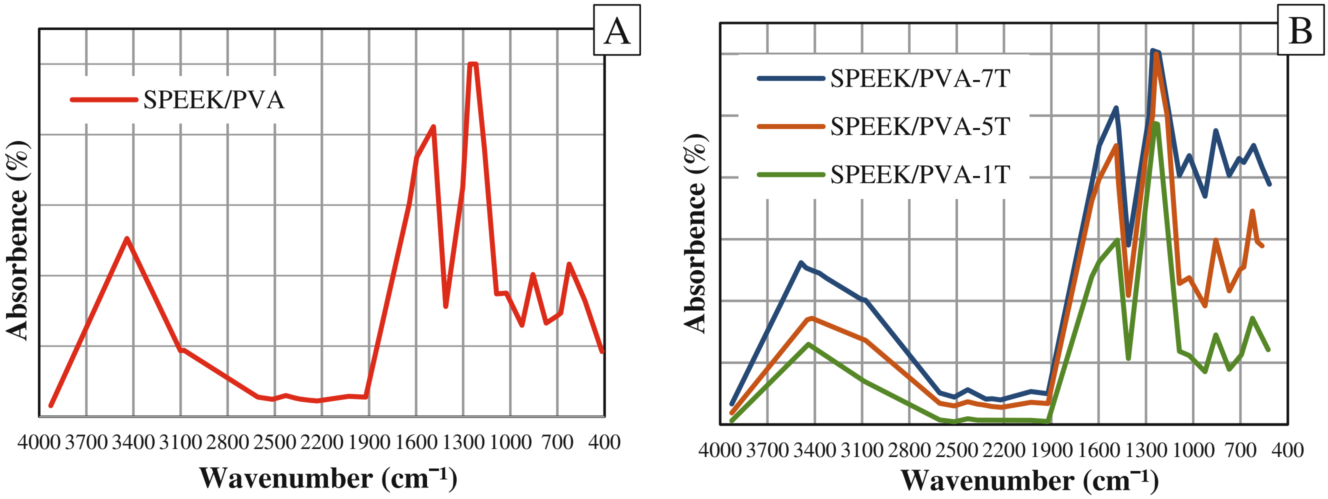

Figure 4. FT-IR spectra of the pristine SPEEK/PVA membrane (A) and TiO_2-doped SPEEK/PVA blend membranes (B).

47.35 MPa. These results show that both doped and undoped membranes have higher tensile strength than Nafion 117, with 5 wt% TiO_2 providing the best mechanical performance. However, lower or higher TiO_2 content negatively impacts mechanical properties. Consistent with these findings, a previous investigation on nano-TiO_2-doped poly(vinylidene fluoride) and phosphorylated PVA composite blend membranes reported a decline in mechanical strength with higher nano-TiO_2 loadings.[40] The 5 wt % TiO_2 doped membrane showed the best performance, with a tensile strength of 29.28 MPa and an elongation ratio of 3.54%. In a comparable study with results aligned with this study, the addition of TiO_2 to a SPEEK membrane significantly affected its mechanical properties. These results highlight that 5 wt% TiO_2 optimized the mechanical properties, while higher concentrations weakened the membrane.[39]

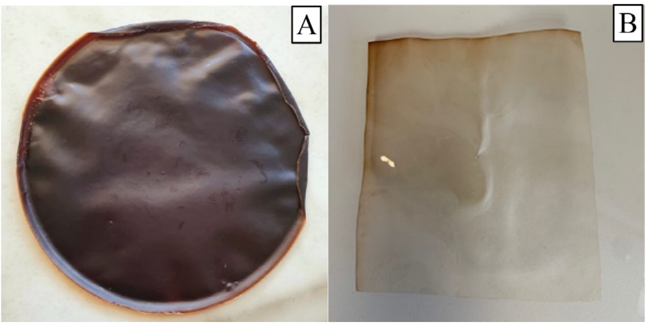

Figure 5. SPEEK/PVA-5T membrane (A) and Nafion 117 membrane (B).

A thermal crosslinking process was employed to enhance the water resistance of the membranes by reducing their water solubility. However, this process can result in a decrease in mechanical stability of the membranes.[51] Table 3 presents the weight loss of the membranes in water at 25 °C. According to the results, thermal crosslinking effectively reduced the water mass loss of the SPEEK/PVA blend membrane from 10.20% to 3.46%, aligning closely with the Nafion 117 membrane, which exhibited a water mass loss of 2.97%. Based on these findings, the optimal thermal crosslinking conditions were determined to be 180 °C for 48 h and to avoid compromising the mechanical properties, higher temperatures and extended durations were not used.

FT-IR analysis

FT-IR spectra of both the pristine SPEEK/PVA blend and the TiO_2-doped SPEEK/PVA blends are presented in Fig. 4. The FT-IR analysis of the SPEEK membrane revealed a peak at 1257.36 cm^{-1}, which corresponds to the symmetric and asymmetric stretching bands of the sulfonate group (S═O). This result is consistent with previous findings, where similar characteristic peaks for SPEEK were observed at 1020–1305 cm^{-1}.[52] Characteristic TiO_2 peaks

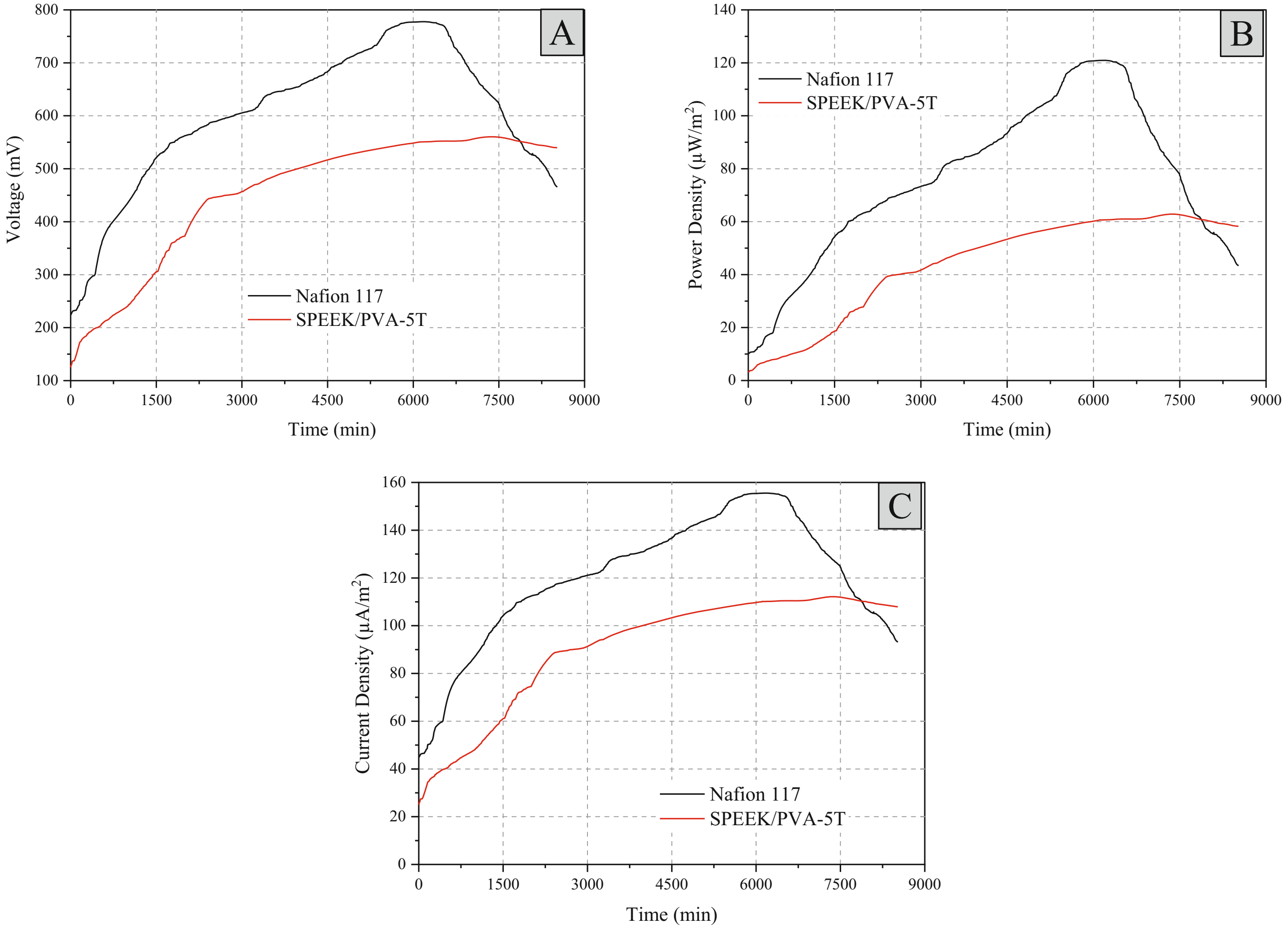

Figure 6. Change of voltage (A), power density (B), and current density with time (C).

were observed in the range of 550–602 cm^{-1}.[53] The analysis showed a distinct peak at 617.109 cm^{-1} indicating that TiO_2 was successfully incorporated into the membrane structure, confirming the presence of the TiO_2 additive.

Performance of SPEEK/PVA-5T and Nafion 117 membranes in MFC

Based on the comprehensive evaluation of all characterization tests and analyses, the SPEEK/PVA-5T membrane demonstrated the most favorable performance. Therefore, performance tests were conducted with the SPEEK/PVA-5T membrane alongside the Nafion 117 membrane using an H-type cylindrical MFC. These membranes are depicted in Fig. 5.

In this system, to correctly compare study values, both the SPEEK/PVA-5T membrane and Nafion 177 membrane performance tests were operated under the same conditions. Experiment results are shown in Fig. 6.

In the presence of electroactive microorganisms, the maximum voltage generated by the SPEEK/PVA-5T membrane reached 560.61 mV, approximately 27.8% lower than that of Nafion 117, which recorded a maximum voltage of 777.14 mV. The highest power density values for SPEEK/PVA-5T and Nafion 117 membrane were calculated as 62.856 and 120.975 $\mu\mathrm{W\,m}^{-2}$, respectively. It is well known that the optimal performance of MFCs are directly proportional to factors like separators (with and without membranes), anode and cathode characteristics along with the role of exoelectrogens used. In this study, electrodes, exoelectrogens and electron donors are the same. Therefore, the difference between the performances may be explained by the differences between the membrane structure. The data in Fig. 2(B) show that the swelling ratio of SPEEK/PVA-5T membrane is almost three times higher than that of Nafion 117 membrane. Increase in swelling ratio means an increase in diffusional resistance against ionic transport and hence a decrease in potential difference between anode and cathode.

The COD concentration and the pH value of the anode chamber were measured at regular intervals and the obtained data are given in Fig. 7. Figure 7(A) shows that the COD removal values obtained from the performance test were calculated as 80.10% and 80.52% for SPEEK/PVA-5T and Nafion 117, respectively. In

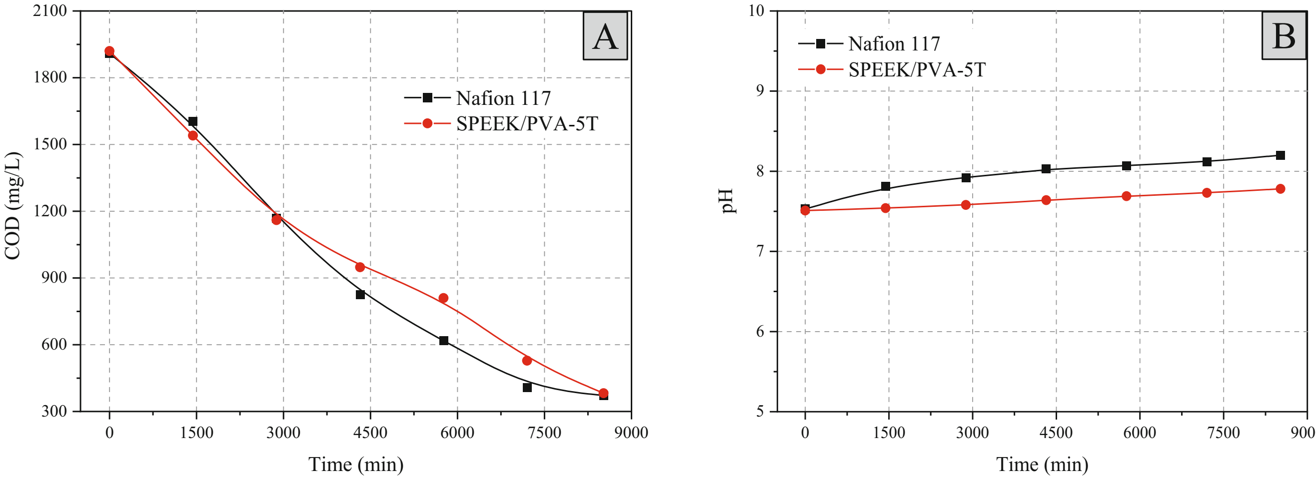

Figure 7. Change of chemical oxygen demand (COD) concentration (A) and anodic pH value (B) with time.

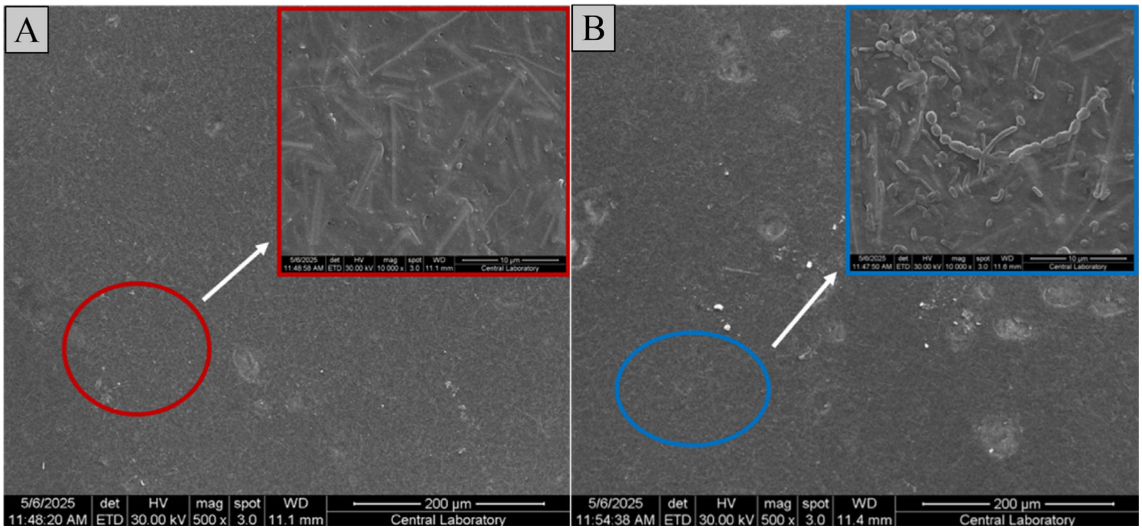

Figure 8. SEM images of SPEEK/PVA membrane before use (A) and after use (B).

addition, these results are comparable to the COD removal values reported in the literature obtained from MFC systems using synthetic wastewater in recent years.[16,39,54,55] pH measurement was carried out by taking a sample from the anode chamber and the results are given in Fig. 7(B) for the SPEEK/PVA-5T and Nafion 117 membranes. For each membrane, pH values were observed to be at neutral levels.

SEM analysis

SEM analysis contributes an excellent overall picture of the surface morphology. This analysis investigated the surface of the SPEEK/PVA-5T membrane and characterized its structure (before and after use). The SEM analysis of the SPEEK/PVA-5T revealed important findings regarding the morphology and potential impact on membrane performance. Figure 8 presents SEM images of this membrane.

The SEM analysis highlighted the presence of abundant populations of TiO_2 and pores on the membrane surface offering insights into the composition and potential functionality. Figure 8(A) represents a smooth and homogeneous surface, indicating the homogeneous dispersion of TiO_2 particles. Moreover, under high magnification (Fig. 8(A)), the SEM image shows the presence of rod-shaped TiO_2 particles. The after-use SPEEK/PVA-5T membrane is covered with a rough layer, as shown in Fig. 8(B). The membrane surface consisted of a bacterial community, especially rod-shaped and coccus bacteria, indicating biofouling occurred on the surface. Also, elemental analysis was performed (after use) to verify the membrane's layer chemical components and identify the major composition of the fouling layer. As shown in Fig. 9, Ti, C, O, Mg, Na, K, Ca and S elements were detected using an SEM–energy-dispersive X-ray (EDX) system.

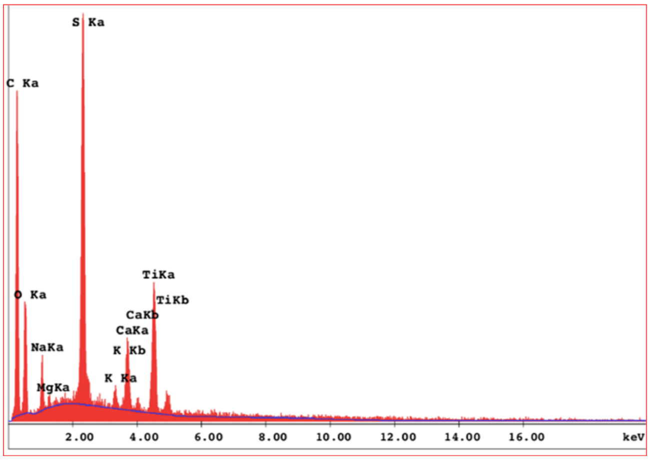

Figure 9. EDX analysis of SPEEK/PVA-5T membrane (after use).

DISCUSSION

Figure 3 shows that the findings confirm that the incorporation of TiO_2 into the membrane structure enhances both WC and IEC. Both TiO_2-doped and undoped membranes synthesized under identical test conditions demonstrated superior performance compared to Nafion 117 which exhibited WC values of 15.82% and IEC values of 0.0751 meq g^{-1}. Furthermore, in Fig. 4, results show the importance of optimizing the additive concentration to achieve balanced performance. These findings suggest that the addition of 5 wt% TiO_2 represents the most optimal configuration for SPEEK/PVA blend membranes. In previous studies, similar trends were observed with TiO_2 incorporation into various membrane structures. For instance, in a study on nanocomposite membranes, the inclusion of nano-TiO_2 in a Nafion membrane increased its proton conductivity from 3.9 to 12.6 mS cm^{-1} compared to the undoped membrane. Finally, synthetic wastewater treatment and electricity generation were investigated in an H-type cylindrical MFC using SPEEK/PVA-5T and Nafion 117 membranes. As a result of this study, the SPEEK/PVA-5T membrane, the maximum voltage, maximum power density and COD removal efficiency were found as 560.61 mV, 62.856 $\mu W\ m^{-2}$ and 80.10% respectively. The maximum voltage and COD removal efficiency values are compared with those from some literature studies in Table 4.

Table 4 shows that COD removal values obtained for the SPEEK/PVA-5T membrane. It can be said to be comparable to the values reported in the literature. Also, the potential values obtained using the SPEEK/PVA-5T membrane are higher than most of the reported values. It has been shown that conductivity of substrate solution (or wastewater), diffusion coefficient, charge transfer rates, activation energy, biochemical processes of the microbial communities, etc., the combined effect of which can significantly alter the MFC power output.[61,62] Differences between the voltage

Table 4. Maximum voltage and chemical oxygen demand (COD) removal efficiency compared with other studies

Substrate	Membrane	Voltage (mV)	COD removal (%)	Ref.
Synthetic wastewater	SPEEK/PVA-5T	560.61	80.10	This study
Synthetic wastewater	TiO_2/SPEEK composite membrane	635	89.70	39
Synthetic wastewater	Fe_3O_4/PES nanocomposite membrane	552.50 ± 29.50	—	54
Synthetic wastewater	CNT modified SPEEK membrane	—	90	55
Molasses wastewater	Modified PVDF	210	66.7	14
Synthetic wastewater	PES with 10 wt% of sulfonated Fe_3O_4	868.09	—	56
Synthetic wastewater	Polypropylene	500	—	57
Domestic wastewater	NSCS PEM	612 ± 4.35	82.48 ± 0.30	58
Petroleum refinery wastewater	Nafion	305	64 ± 4	59
Synthetic wastewater	PEM constituting 5% goethite and natural clay	73.2 ± 2.14	87.7 ± 5.8	60

SPEEK/PVA, sulfonated poly(ether ether ketone)/poly(vinyl alcohol); PEM, proton exchange membrane; TiO_2, titanium dioxide.

and COD removal values for different membrane may be explained by the differences between the compositions of the wastewater used in different studies as electron donor medium. In some studies yeast and glucose[39] were used whereas in some other studies sodium acetate,[54] synthetic dairy wastewater[55] or molasses wastewater[14] were used. Another important reason is the differences between the structure of the membranes used in different studies. Larger specific surface area and richer and finer pores are more beneficial for microorganisms to adhere to the membrane surface and, thus, increase the growth space of the anode biofilm and improve the electron transfer of the whole system.

This study aims to develop a chemically and mechanically stable membrane that can be an alternative to the expensive Nafion membranes, with high ionic conductivity and low cost. Depending on these results it can be said that SPEEK/PVA-5T membrane can be a good alternative for Nafion 117.

CONCLUSIONS

Characterization tests revealed that the SPEEK/PVA-5T membrane exhibited superior WC, IEC and proton conductivity compared to the commercial Nafion 117 membrane, underscoring its potential as a viable alternative. The results of this investigation indicate that the SPEEK/PVA-5T membrane is a promising candidate for future development as a substitute for Nafion in MFC applications. This study stands out for its innovative use of unique polymer blends and represents the first report of the incorporation of TiO_2 into such a membrane for MFCs. Overall, the SPEEK/PVA-5T membrane demonstrates strong potential for efficient power generation in MFC systems. Moreover, its nontoxic nature toward microorganisms and its ability to enhance system performance further support its recommendation for future MFC research and applications.

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CONFLICT OF INTEREST

The authors declared no conflict of interest.

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