

Review

Effect of Sulfonated Inorganic Additives Incorporated Hybrid Composite Polymer Membranes on Enhancing the Performance of Microbial Fuel Cells

Gowthami Palanisamy, Sadhasivam Thangarasu *  and Tae Hwan Oh * 

School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea

* Correspondence: sadhasivam.nano@gmail.com (S.T.); taehwanoh@ynu.ac.kr (T.H.O.)

Abstract: Microbial fuel cells (MFCs) provide considerable benefits in the energy and environmental sectors for producing bioenergy during bioremediation. Recently, new hybrid composite membranes with inorganic additives have been considered for MFC application to replace the high cost of commercial membranes and improve the performances of cost-effective polymers, such as MFC membranes. The homogeneous impregnation of inorganic additives in the polymer matrix effectively enhances the physicochemical, thermal, and mechanical stabilities and prevents the crossover of substrate and oxygen through polymer membranes. However, the typical incorporation of inorganic additives in the membrane decreases the proton conductivity and ion exchange capacity. In this critical review, we systematically explained the impact of sulfonated inorganic additives (such as (sulfonated) sSiO₂, sTiO₂, sFe₃O₄, and s-graphene oxide) on different kinds of hybrid polymers (such as PFSA, PVDF, SPEEK, SPAEK, SSEBS, and PBI) membrane for MFC applications. The membrane mechanism and interaction between the polymers and sulfonated inorganic additives are explained. The impact of sulfonated inorganic additives on polymer membranes is highlighted based on the physicochemical, mechanical, and MFC performances. The core understandings in this review can provide vital direction for future development.

Keywords: microbial fuel cell; bioenergy; water treatment; membrane; separator; hybrid polymer composite; sulfonation; additives



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1. Introduction

As the world's population grows, resulting in the overconsumption of energy, mostly from fossil fuels, it has a detrimental influence on the environment through green gas emissions, resulting in global warming and a changing climate and biosphere emergency [1–3]. We need cleaner energy technology to solve this problem as soon as possible. This includes saving energy by making it more efficient, using fewer fossil fuels, and making environment-friendly energy sources more accessible. Accordingly, renewable energy sources, such as water, sun, wind, biomass, and geothermal technologies, have been addressed as an alternative to conventional energy sources [4–6]. Therefore, scientists worldwide have come up with different ways to convert and store electrochemical energy, such as fuel cells [7–9], batteries [10,11], and electrochemical capacitors [12,13]. Electrochemical energy conversion and storage technologies have been considered an alternative due to their eco-friendly and sustainable routes [14]. Over the past several decades, fuel cell technologies have gained considerable attention because of their enhanced energy conversion efficiency, energy density, and reliability, and they work continuously until there is an endless supply of fuel and oxygen [8,15,16]. Based on the electrolyte, fuels, and operating temperature, the fuel cells are classified into proton exchange membrane fuel cells [17], alkaline fuel cells [18], solid oxide fuel cells [19], phosphoric acid fuel cells [20], microbial fuel cells (MFCs) [21–23], enzymatic fuel cells [24], direct methanol fuel cells [25], molten-carbonate fuel cells [26], direct ethanol fuel cell [27], unitized regenerative fuel

cells [28,29], direct borohydride fuel cells [30], direct ethylene glycol fuel cells [31], direct glycerol fuel cells [32], and direct formic acid fuel cells [8,33].

Among the different fuel cell technologies, the MFC is considered an excellent energy system [34–37]. The most exciting advantage of MFCs is generating electricity via biological microorganisms using wastewater [38–40], such as industrial wastewater [41–43]. Generally, the MFC generates electricity using organic waste [44,45]. The MFC has been widely considered in various sectors, such as environmental science, engineering, electrochemistry, and energy [46,47]. In terms of application, an MFC has been widely believed to produce biohydrogen, bioelectricity, and biosensors and also be used in bioremediation processes [48–51]. During MFC operation, MFC allows for simultaneous bioenergy production and bioremediation in a single device. The MFC usually emits carbon dioxide during unit cell operation. However, the MFC system was carbon-neutral for generating energy [52–54]. Based on the unit cell alignments, the MFCs have been classified into different categories, such as stacked, up-flow, double-chamber, and single-chamber MFCs [55,56]. Figure 1 [34] depicts the dual-chamber MFC process schematically. Here, the anode chamber and the cathode chamber have been separated by the ion exchange membranes [57–59]. In MFCs, the center part of the ion exchange membrane has a predominant role during the unit cell operation, such as ion transportation, controlling the substrate crossover, and prohibiting the oxygen crossover [60–64]. The functioning of electron transportation and ion transportation in MFCs is similar to the proton exchange membrane fuel cell [65,66]. In MFCs, electricity is commonly derived using microbial sources. In MFCs, the microorganism breaks down organic matter to make electrons, protons, and carbon dioxide as byproducts [67,68]. As shown in Figure 1, an electron is transferred to the cathode using an external circuit, and protons are transported to the cathode using a proton exchange membrane from the anode side to the cathode side. At the cathode, oxygen, protons, and electrons combine to form water, a byproduct of an oxygen reduction reaction (Figure 1). Some examples of oxidation of organic matter through microorganisms in an anode chamber are as follows [69–71]:



The example of cathode chamber reaction is as follows:

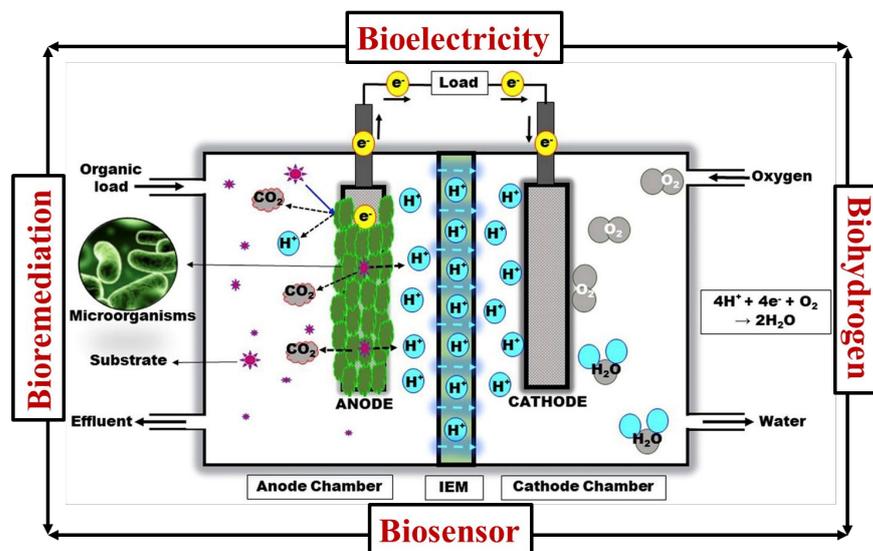
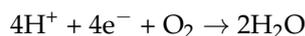


Figure 1. A schematic representation of dual-chambered microbial fuel systems reaction process and applications. Reproduced from [34], with permission from Elsevier, 2019.

The main things that affect the performance of MFCs are the components, the process variables, and the way the unit cells are set up [40,72,73]. In MFCs, the proton exchange membrane is one of the most critical components to attaining excellent performance for generating electricity and wastewater treatment [74–76]. Perfluorosulfonic-acid-based commercial membranes (e.g., Nafion and CMI 7000) have been used as an ideal proton exchange membrane candidate for MFC applications because of their proton exchange capability and stability [77–81]. Commercial membranes have certain drawbacks, such as a high production cost, high oxygen/substrate crossover, biological accumulation, biofouling, and deprivations [82,83]. Various kinds of polymer membranes have been developed in different categories, such as composite membranes, blend membranes, reinforced membranes, sandwich-type membranes, and crosslinked membranes [84–92], to overcome these issues.

Among the various approaches, incorporating inorganic nanomaterials in the polymer matrix to create a hybrid composite membrane is an important consideration for the MFC. Inorganic nanomaterials are frequently used in membranes to improve their dimensional, mechanical, thermal, and chemical properties. In MFCs, the inorganic nanoparticles are used to control the fuel crossover and change the physicochemical properties of the membrane, in addition to making it more stable. The incorporated inorganic nanomaterial fillers are classified into various categories, such as inert hygroscopic, proton conductor, and proton-conducting properties with hydrophilic nature [93–95]. In most cases, the inorganic nanofillers control the membrane's fuel crossover, dimensional stability, and mechanical strength [96–99]. However, incorporating inorganic nanofillers can significantly affect proton transport behavior in most membranes, which is a disadvantage of inorganic nanofillers. To improve the efficacy of inorganic nanofillers, surface modification and functionalization have been executed for different kinds of inorganic nanofillers and utilized for MFC applications. Among the various changes and functionalization, introducing the sulfonic acid functional group ($-\text{SO}_3\text{H}$) in the inorganic nanomaterials is an excellent way to promote proton conductivity and decrease the fuel crossover in the membrane. The sulfonic acid functional group enhances the hydrophilicity of the membrane and also holds the membrane's dimensional stability, which is a significant benefit of using sulfonated inorganic additives. In addition, the sulfonation site in the inorganic fillers makes it possible for hydrogen bonds to form between polymers and inorganic materials. The membrane contains higher dimensional stability due to its hydrophilic nature. An acid functional group can effectively transfer the protons from the anode to the cathode via the vehicular (diffusion) and Grotthuss (hopping) mechanisms. This phenomenon generates more ionic channels and carriers for efficient proton transport. As a result, many different kinds of inorganic additives have been tried for MFC applications. The sulfonation of nanoparticles (NPs) and nanomaterials has positively tuned the properties, such as water uptake (WU), dimensional stability, ion exchange capacity (IEC), proton conductivity (PC), biofouling, and mechanical stability and performance of membranes, for MFC applications. This review systematically explained the impact of nonsulfonated and sulfonated inorganic additives on different kinds of polymers for MFC applications. According to the developments of sulfonated inorganic additives for MFC applications, the evaluation is described in five sections; namely, sulfonated silica incorporated polymer membrane, sulfonated TiO_2 containing polymer membrane, sulfonated graphene oxide containing polymer membrane, sulfonated Fe_3O_4 containing polymer membrane, and different kinds of sulfonated additives in polymer membrane.

2. Sulfonated Silica Incorporated Polymer Membrane for MFC Applications

Inorganic silica (SiO_2) has recently been widely regarded as an excellent nanofiller material in membranes for various energy devices [100–103]. Generally, the inorganic SiO_2 contains considerable properties for membranes, such as an increased surface area with excellent physical, chemical, and thermal properties [104]. Moreover, the incorporation of inorganic SiO_2 into the polymer matrix enhances the PC of the composite membrane due to the high water-holding property of SiO_2 [105]. Different ideas about SiO_2 have

been made and studied in this context for use in MFC membranes. Kircheva et al. investigated the MFC performance of a low-cost microporous polyethylene (PE)/silica (PE-Si) membrane in an air-cathode MFC, finding that the PE-Si membrane performed similarly to the Nafion 117 membrane under different conditions using nonparametric analysis (Mann–Whitney) [106]. In another approach, composite membranes have been developed by SiO₂-polyvinyl chloride (PVC) by solution casting method [107]. The PC of the composite membrane has been increased by incorporating hygroscopic silica gel due to its high WU property and the inclusion of the desired ratio of citric acid and phosphotungstic acid (PWA). Increasing the concentration of silica increases the IEC and WU capacities. Though particle agglomeration has increased the silica concentration beyond the limit, this has decreased the mechanical strength. The maximum power density (PD) obtained was 43.91 mW cm⁻² for the composite membrane containing 5% silica with 5% PWA [107].

Angioni et al. introduced mesoporous silica (SBA-15) and modified it with propylsulfonic groups (10 and 50 mol.% of SBA-SO₃H) as fillers into the Nafion membrane [108]. The prolonged study of MFCs using wastewater showed that the Nafion-SBA15–SO₃H (10 mol.%) membrane exhibited higher PD (380 mW m⁻³) than the Nafion membrane with higher COD removal efficiency (95%) and enhanced coulombic efficiency (CE) (34%). Moreover, SBA15-SO₃H-based fillers protect the surface of the composite membrane from biofouling. Thus, the mesoporous SBA-SO₃H fillers in Nafion could be used to develop composite membranes for MFC wastewater treatment [108]. Incorporating inorganic additives enhances the PC of the composite membrane at high temperatures [104]. In case of low temperature (30 °C), the PC of the composite membrane has been reduced [104,109,110]. Hence, sulfonation of the inorganic additives has been incorporated to increase PC at low temperatures. In this way, Sivasankaran et al. fabricated a PEM comprising sulfonated SiO₂ (sSiO₂—2.5, 5, 7.5, and 10%) into sulfonated polystyrene ethylene butylene polystyrene (SSEBS) for single-chamber MFC (SCMFC) [104]. The interaction between sSiO₂ and SSEBS is shown in Figure 2a. By increasing the s-SiO₂ content in the composite membrane, the IEC (3.015 meq/g) and PC (0.321 S/cm) (Figure 2b) increased up to 7.5% s-SiO₂ concentration. In similar conditions, the IEC and PC of pure SSEBS are 1.825 meq/g and 1.52 × 10⁻² S/cm, respectively. It makes the s-SiO₂ concentration even higher (over 7.5%) and decreases the PC of the membrane because too much s-SiO₂ causes it to clump together. Because of this, the composite membrane's ability to take in water worsens, making it harder for protons to pass through membranes. Due to its higher PC and lower oxygen permeability, the SSEBS-s-SiO₂ 7.5% composite membrane has been found to improve the performance of the SCMFC (Figure 2c,d); 7.5% sSiO₂ in the SSEBS composite membrane resulted in a higher PD of 1209 ± 17 mW m⁻² [104]. In another study, Sivasankaran and Sangeetha prepared (Figure 2e,f) a sSiO₂-containing composite membrane with SPEEK [105] instead of SSEBS polymer for SCMFC. The presence of sSiO₂ in the SPEEK polymer enhanced the WU, IEC, and PC of the SPEEK-sSiO₂ membrane. Therefore, MFCs with a SPEEK-sSiO₂ membrane generated a power output of 1008 mW m⁻² (Figure 2g), three times more than Nafion 115 (320 mW m⁻²). Moreover, the SPEEK-sSiO₂ membrane revealed excellent unit cell performance compared to the SPEEK (680 mW m⁻²) and SPEEK-SiO₂ (nonsulfonated SiO₂-802 mW m⁻²) membranes [105]. Moreover, the same research group investigated the effect of a SPEEK-SiO₂ nanocomposite membrane on microbial community via tubular MFC in generating electricity by treating sewage wastewater [111]. It was also observed that sulfonated inorganic filler increased the PC of composite membrane because the sulfonated organic–inorganic materials in the membrane enhanced the performance [111]. Table 1 presents the physical and chemical properties and evaluation results of sulfonated silica incorporated polymer membranes for MFC applications.

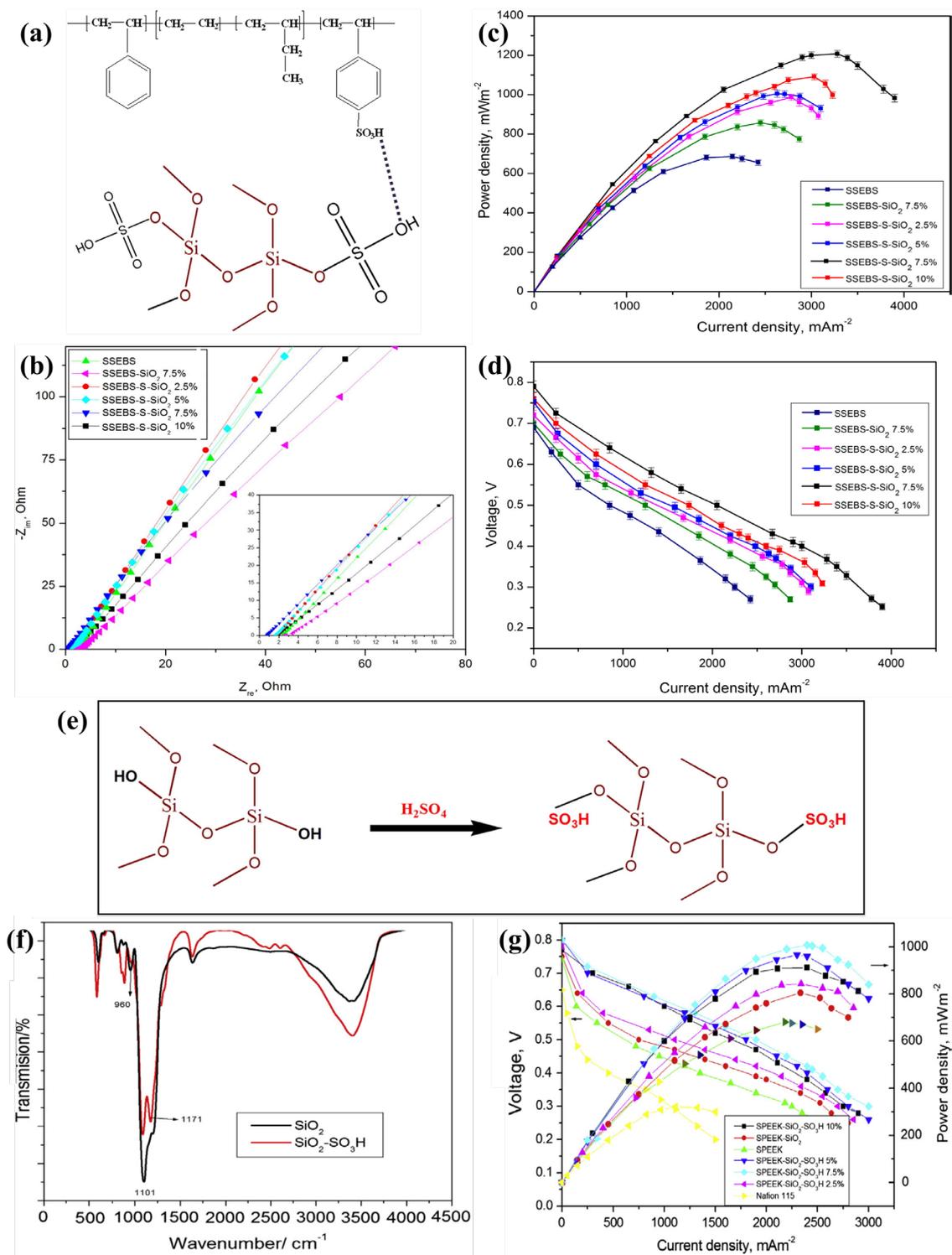


Figure 2. (a) A graphical representation of SSEBS polymer and sSiO₂ inorganic filler interaction. (b) Nyquist plots, (c) power density, and (d) polarization curves of SSEBS, SSEBS/SiO₂ (7.5%), and SSEBS/sSiO₂ (2.5, 5, 7.5, and 10%) membranes. Reproduced from [104], with permission from Elsevier, 2016. (e) Preparation of sSiO₂, (f) FT-IR of SiO₂ and sSiO₂, and (g) polarization curve and power density of Nafion 115, SPEEK, SPEEK-SiO₂, and SPEEK-sSiO₂ membranes. Reproduced from [105], with permission from Elsevier, 2015.

Table 1. Physicochemical properties and performance evaluation results of sulfonated silica incorporated polymer membrane for MFC applications.

IA	Polymer	WU (%)	IEC(meqg ⁻¹)	PC S/cm)	K0 (cms ⁻¹)	IR (Ω)	PD (mWm ⁻²)	CE (%)	Ref.
	Nafion			0.085					
Mesoporous silica (SBA-15)	Nafion			0.028					[108]
SBA-SO ₃ H10	Nafion			0.062				34	
SBA-SO ₃ H50	Nafion			0.088					
	SSEBS	164 ± 7	1.825		3.5 × 10 ⁻⁵	66	680 ± 13	75	
SiO ₂ -7.5%	SSEBS	185 ± 8	1.622		0.9 × 10 ⁻⁵	60	852 ± 11	78	
S-SiO ₂ -2.5%	SSEBS	175 ± 10	1.990		0.98 × 10 ⁻⁵	55		82	
S-SiO ₂ -5%	SSEBS	187 ± 9	2.55		0.8 × 10 ⁻⁵	45		80	[104]
S-SiO ₂ -7.5%	SSEBS	210 ± 8	3.015	3.21 × 10 ⁻²	0.75 × 10 ⁻⁵	37	1209 ± 17	85	
S-SiO ₂ -10%	SSEBS	200 ± 11	2.821		0.67 × 10 ⁻⁵	39		83	
	Nafion	22	0.982	2 × 10 ⁻²	1.6 × 10 ⁻⁴		290 ± 7		
	SPEEK	23	1.12		3 × 10 ⁻⁶	71 ± 3	680	75 ± 4	
SiO ₂ -5%	SPEEK	39	1.41		0.9 × 10 ⁻⁶	62 ± 2	802	79 ± 4	
S-SiO ₂ -2.5%	SPEEK	35	1.65		1.2 × 10 ⁻⁶	55 ± 2	864	85 ± 5	
S-SiO ₂ -5%	SPEEK	40	1.73		1 × 10 ⁻⁶	50 ± 1	912	87 ± 6	[105]
S-SiO ₂ -7.5%	SPEEK	42	1.80	1.018 × 10 ⁻²	0.84 × 10 ⁻⁶	46 ± 0.5	1008 ± 17	90 ± 7	
S-SiO ₂ -10%	SPEEK	37	1.74		0.7 × 10 ⁻⁶	52 ± 1	810	85 ± 6	
		22		3.0 × 10 ⁻²	1.6 × 10 ⁻⁵		320 ± 6		
	SPEEK	37 ± 0.3	1.15 ± 0.06	0.96 × 10 ⁻²	2.2 × 10 ⁻⁶	39	59 ± 1.2		
2.5wt% S-SiO ₂	SPEEK	38 ± 0.5	1.34 ± 0.03	0.99 × 10 ⁻²	1.74 × 10 ⁻⁶	37	72 ± 1.6		
5wt% S-SiO ₂	SPEEK	39 ± 0.4	1.54 ± 0.05	1.14 × 10 ⁻²	1.64 × 10 ⁻⁶	32			[111]
7.5wt% S-SiO ₂	SPEEK	40 ± 0.6	1.82 ± 0.08	1.24 × 10 ⁻²	1.42 × 10 ⁻⁶	29	154 ± 1.5		
10 wt% S-SiO ₂	SPEEK	39 ± 0.3	1.71 ± 0.04	1.1 × 10 ⁻²	1.49 × 10 ⁻⁶	34			
	Nafion	22 ± 0.4	1.2 ± 0.05	0.85 × 10 ⁻²	2.42 × 10 ⁻⁶	45	145 ± 1.6		

IA—inorganic additives, WU—water uptake, IEC—ion exchange capacity, PC—proton conductivity, K0—oxygen mass transfer coefficient, IR—internal resistance, PD—power density, CE—coulombic efficiency.

3. Sulfonated TiO₂ Containing Polymer Membrane for MFC Applications

The inorganic nanofillers of TiO₂ and its modified version gained potential advantages for developing organic–inorganic hybrid composite membranes due to their hygroscopic, chemical properties and inbuilt antibacterial effect [112,113]. Membrane fouling has been reduced in the composite membrane containing TiO₂ due to its hydrophilic properties, which increase the membrane surface hydrophilicity, thus decreasing the hydrophobic interaction between microorganisms and the membrane surface [114]. Christophe Pagnout et al. studied the electrostatic interaction between *Escherichia coli* and TiO₂. In this case, at neutral pH, the TiO₂ does not show any toxicity toward *E.coli*. Still, it exhibits toxicity in acidic and alkaline pH conditions due to the positive and negative charges of TiO₂ and bacterium, respectively [115]. Introducing TiO₂ and sulfonated TiO₂ (sTiO₂) provides considerable benefits for developing the hybrid membrane for various energy systems [116–120]. Bajestani and Mousavi developed a Nafion-TiO₂-1 wt% membrane using different solvents (NMP, DMAc, and DMF) [112]. The characteristic membrane behaviors were investigated along with the impact of casting solvents. The solvents used in membrane preparation are responsible for the membrane morphology through their volatility and polymer–solvent–NP interaction. Nafion-TiO₂ with DMF demonstrated strong hydrogen bonding interactions and higher porosity among the tested solvents. Thus, the Nafion-TiO₂ in the DMF solvent membrane showed higher WU (51%), PC (0.0126 S/cm), and IEC (1.32 meqg⁻¹). Moreover, the enhanced PC of Nafion-TiO₂ with DMF solvent exhibits an increased OCV (330 mV) of MFCs at steady-state conditions [112].

Sulfonated polyether ether ketone (SPEEK) is an excellent candidate among hydrocarbon polymers due to its low cost and higher chemical and mechanical stability [121,122]. The degree of sulfonation in SPEEK is proportional to the membrane's PC [120]. However, the increased amount of $-\text{SO}_3\text{H}$ functional group in the SPEEK membrane increased the WU and swelling ratio, reducing the membrane's mechanical stability [122]. To address the issues, various inorganic fillers, including TiO_2 , were introduced to modify the properties of SPEEK membranes [123]. In this connection, Venkatesan and Dharmalingam prepared a SPEEK- TiO_2 composite membrane using the rutile structure of TiO_2 for MFC applications [124]. An increased oxygen mass transfer coefficient and cation transport behavior were observed for the composite membrane. Among different concentrations of TiO_2 (2.5, 5.0, 7.5, and 10%), the 7.5% TiO_2 in SPEEK composite membrane showed efficient IEC, PC, antifouling properties, and PD. It has been seen that increased TiO_2 content (10% TiO_2) exhibits a blocking effect and controls the ionic channels, which affects the PC of the membrane [124]. In another approach, different ratios of TiO_2 (2.5, 5, 7.5, and 10%) in SPEEK membranes were developed for generating electricity from dairy wastewater [125]. Among different ratios, SPEEK with a 5% TiO_2 composite membrane showed increased WU (31%) and IEC (1.71 meqg^{-1}). From the MFC performances, it has been identified that SPEEK with a 5% TiO_2 composite membrane showed increased PD (1.22 Wm^{-2}) and voltage (0.635 V). Moreover, the hybrid composite membrane exhibits a high COD removal efficiency [125]. The Ti-based compounds of perovskite oxides, such as strontium titanate (SrTiO_3), have also been used as filler for their high hydrophilic nature that enhances the WU property [126–128]. By means of this, silica particles can improve the homogenous dispersivity of the polymer matrix. When surface-modified nanofillers are added to the polymer matrix, they make the membrane stronger than when unmodified nanofillers are added. Bhowmick et al. incorporated the modified SrTiO_3/Si and TiO_2/Si and nanofillers into the PVA polymer matrix for fabricating PEM [126]. The base polymer PVA possesses high hydrophilic properties and film-forming ability due to the cross-linking of the available $-\text{OH}$ groups. SrTiO_3/Si -PVA and TiO_2/Si -PVA composite membranes generated PDs of 5.39 ± 0.27 and $6.16 \pm 0.31 \text{ Wm}^{-3}$, respectively. The induced PDs were comparable to Nafion and 30 times less expensive for developing the composite membrane [126]. Considering cellophane as the base material for membrane developments provides an alternative option for generating electricity and pollutant removal using MFCs. In this case, a 1:1 ratio mixed combination of ZnO and TiO_2 NPs (0.03%) was incorporated in the cellophane and further altered with the bio-inspired polydopamine [129]. This combination has been effectively considered because of its novel, cost-effective, antibiofouling, and self-cleaning properties. Power generation was increased during MFC operation by increasing cation transport during the oxidation process via PDA modifications and catalyst mixing of the modified membrane. In addition to this, the membrane surface fouling and lifespan were reduced by the increased hydrophilic property of membrane modifications [129].

Its surface properties have been modified in multiple ways to enhance the efficiency of TiO_2 NPs in membranes. Besides creating more proton transport channels, the surface modification of TiO_2 , primarily sulfonation, also acts as a proton carrier vehicle owing to its negative charge [130,131]. However, due to the neutral charge, metal oxides ($-\text{OH}$ group) and water molecules generated proton transport pathways [131]. In addition, the hydrophilic sulfonic acid groups exchanged the hydroxyl group of TiO_2 during sulphonation that further enhancing the antibiofouling characteristic of the composite membrane [132]. In this view, the impact of sulfonated TiO_2 (sTiO_2) has been evaluated using a SPEEK polymer membrane [133]. The sTiO_2 in the composite enhances PC and reduces oxygen diffusion. The results showed that MFCs with SPEEK- sTiO_2 (7.5 wt.%) membrane generated an excellent PD of 1202.5 mW m^{-2} with a reduced internal resistance of 37Ω [133]. The same research group prepared a novel SPEEK-based composite membrane with hydrothermally synthesized sulfonated titanium nanotube (S-TNT) for enhancing the membrane lifespan, PC and antibiofouling properties for electricity generation through tubular MFC (Figure 3) [130]. The incorporated hollow S-TNT has a high water-holding capacity that

helps to increase the proton transport mechanisms. By using tubular MFC (300 mL), the maximum PD of 121 mWm^{-2} (with 79.37% COD removal) was obtained for the SPEEK/S-TNT (7.5%) composite membrane. The higher performance is mainly possessed by a high IEC value of 3.2 meqg^{-1} with decreased internal resistance (30Ω) [130]. Another approach was made with novel sulfonated polystyrene–ethylene–butylene–polystyrene and sulfonated TiO_2 (SPSEBS/s TiO_2) nanocomposite membranes as PEM for MFC applications [131]. The membrane PC was enhanced by sulfonating the inorganic TiO_2 nanofiller and delivered the highest PD of $1345 \pm 17 \text{ mW m}^{-2}$ for SPSEBS/STiO₂ 7.5%, which was found to be 124% higher than MFCs with pristine SPSEBS membrane [131]. For evaluating MFC performance, a combination of SPSEBS polymer with various percentages of synthesized S-TNT was used, as well as statistical optimization (Box–Behnken factorial design) of operational parameters (catalyst concentration, external resistance, and substrate type) [134]. Here, the STNT in the composite membrane improves hydrophilicity, mechanical stability, and PC with the highest antibiofouling property in MFC application [134]. Cost-effective polyvinylidene fluoride (PVDF) polymers have been considered a membrane candidate for MFC applications. PVDF is also considered a base polymer material for preparing PEM due to its better thermal and chemical properties [135–137]. To enhance the PC of PVDF, modifying PVDF through a polymer grafting method in which sodium styrene sulfonate directly reacts with ozone-preactivated PVDF powder and is grafted into leading chains resulted in the development of PVDF-g-PSSA membrane with enhanced mechanical and chemical stability with PC [138]. Although the hydrophobic nature of PVDF causes membrane biofouling on the membrane surface in PVDF-g-PSSA membranes, this makes them not suitable for long-term operation in MFCs [138]. Hence, Li et al. created s TiO_2 by grafting sulfonic groups onto TiO_2 and embedding it in PVDF-g-PSSA membranes to create a s TiO_2 -PSSA composite membrane with enhanced PC and antibiofouling properties using a solution casting technique [139]. Transmission electron microscopy (TEM) analysis (Figure 4a,b) has shown that PPSSA and s TiO_2 -PPSSA have both hydrophilic and hydrophobic regions and ionic aggregation. The hydrophilic region refers to darker regions, and the hydrophobic region refers to brighter areas. Here, the hydroxyl groups in the inorganic TiO_2 filler have been substituted with a sulfonic acid group in s TiO_2 . Therefore, adding of s TiO_2 increased the hydrophilicity of the STiO₂-PSSA composite membrane, which made the membrane better at absorbing water. As a result of the interdependent effect of Grothuss and vehicle mechanisms, the development of proton transport pathways increases membrane PC (Figure 4c). The s TiO_2 -PSSA composite membrane stability and the antibiofouling property have been evaluated through MFC operation for 2 months with their obtained PDs and polarization curves (Figure 4d). The fouled composite membrane demonstrated an excellent PD and a 91% higher COD removal efficiency than the Nafion 117 membrane [139]. Table 2 displays the physicochemical properties and performance evaluation results of polymer membranes with different kinds of TiO_2 added for MFC applications.

Table 2. Physicochemical properties and performance evaluation results of sulfonated TiO_2 containing polymer membrane for MFC applications.

IA	Polymer	WU (%)	IEC (meqg ⁻¹)	PC S/cm	K0 (cms ⁻¹)	IR (Ω)	PD (mWm ⁻²)	CE (%)	COD (%)	Ref.
S-TiO ₂ -5%	SPEEK	37	0.99		0.7×10^{-6}					
TiO ₂ -5%	SPEEK	25	0.75		0.7×10^{-6}					
	SPEEK	20	0.9		3×10^{-6}					
S-TiO ₂ -2.5%	SPEEK	32	0.95		0.5×10^{-6}					[133]
S-TiO ₂ -7.5%	SPEEK	39	1.05	1.382×10^{-2}	0.8×10^{-6}	37	1202.5			
S-TiO ₂ -10%	SPEEK	38	0.94		0.87×10^{-6}					
	Nafion	22		0.30×10^{-2}	1.6×10^{-5}	125	300			

Table 2. Cont.

IA	Polymer	WU (%)	IEC (meqg ⁻¹)	PC S/cm	K0 (cms ⁻¹)	IR (Ω)	PD (mWm ⁻²)	CE (%)	COD (%)	Ref.
	SPEEK	37.2	1.8	0.97×10^{-2}	2.2×10^{-6}	39	59			
S-TNT-2.5%	SPEEK	37.9	2.5	1.1×10^{-2}	1.74×10^{-6}	35	70			
S-TNT-5%	SPEEK	38.5	2.8	1.24×10^{-2}	1.54×10^{-6}	33				
S-TNT-7.5%	SPEEK	39	3.2	1.37×10^{-2}	1.32×10^{-6}	30	121	51 ± 2	79.37	[130]
S-TNT-10%	SPEEK	38.2	2.9	1.0×10^{-2}	1.49×10^{-6}	37				
	Nafion	22	1.2	0.81×10^{-2}	2.4×10^{-6}	45	117			
S-TiO ₂ -7.5%	SPEEK	37.6	2.5	1.18×10^{-2}	1.42×10^{-6}	35	102			
	SPSEBS	163 ± 3	1.89	1.52×10^{-2}	3.5×10^{-5}	66 ± 4	695 ± 7	75 ± 3		
TiO ₂ -7.5%	SPSEBS	170 ± 5	1.62	1.08×10^{-2}	0.8×10^{-5}	60 ± 3	835 ± 8	72 ± 2		
S-TiO ₂ -2.5%	SPSEBS	185 ± 8	2.25	1.75×10^{-2}	0.88×10^{-5}	55 ± 2	975 ± 11	80 ± 4		
S-TiO ₂ -5%	SPSEBS	200 ± 9	3.02	2.51×10^{-2}	0.7×10^{-5}	45 ± 1	1200 ± 15	83 ± 3		[131]
S-TiO ₂ -7.5%	SPSEBS	220 ± 11	3.35	3.57×10^{-2}	0.64×10^{-5}	35 ± 0.8	1345 ± 17	87 ± 4		
S-TiO ₂ -10%	SPSEBS	218 ± 10	3.02	2.72×10^{-2}	0.60×10^{-5}	37 ± 0.5	1105 ± 13	85 ± 5		
	PVDF-g-PSSA	25 ± 0.2		0.046 ± 0.003		243.95	106.67		85	
TiO ₂ -1%	PVDF-g-PSSA	28.3 ± 0.3		0.041 ± 0.002		309.67	98.18		86	
S-TiO ₂ -1%	PVDF-g-PSSA	33.2 ± 0.2		0.048 ± 0.003						
S-TiO ₂ -2.5%	PVDF-g-PSSA	36.4 ± 0.2		0.053 ± 0.002						[139]
S-TiO ₂ -5%	PVDF-g-PSSA	40.9 ± 0.1		0.067 ± 0.002		224.24	130.54		91	
S-TiO ₂ -7.5%	PVDF-g-PSSA	32.6 ± 0.2		0.052 ± 0.003						
	Nafion 117	20 ± 0.1		0.078 ± 0.003		210.57	132.02		74	

IA—inorganic additives, WU—water uptake, IEC—ion exchange capacity, PC—proton conductivity, K0—oxygen mass transfer coefficient, IR—internal resistance, PD—power density, CE—coulombic efficiency.

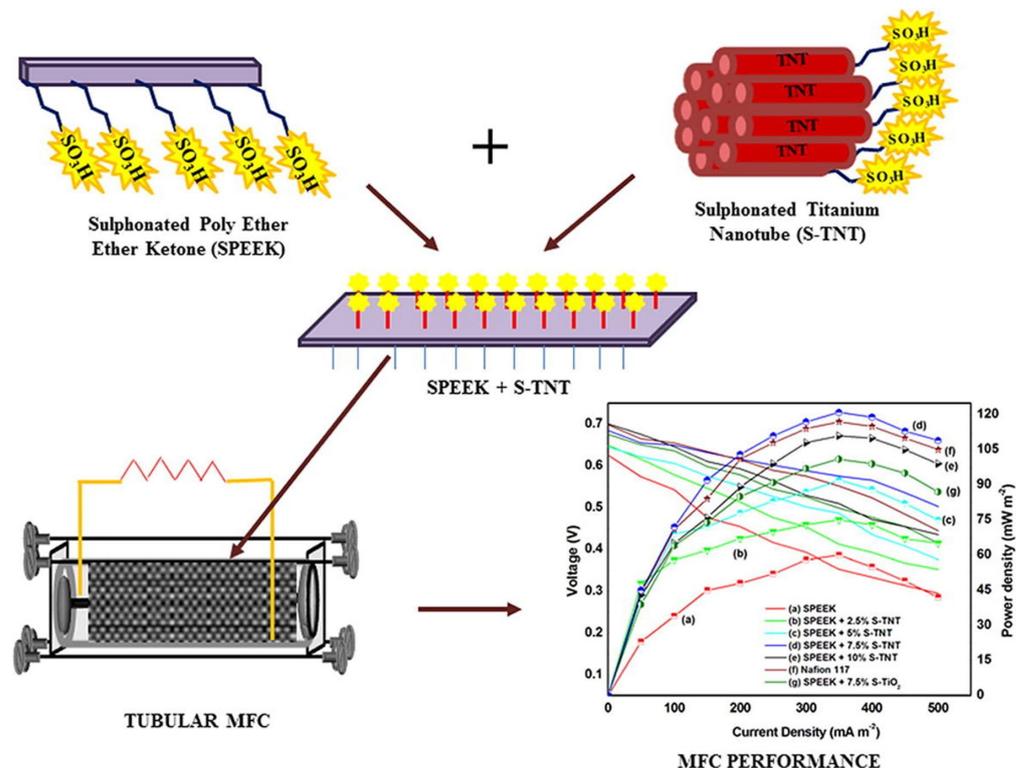


Figure 3. A schematic representation of sulfonated PEEK and STiO₂ nanotube composite membrane developments for tubular MFC and MFC performances (polarization curves and power density) of sPEEK, SPEEK with different ratios of STiO₂ nanotube (2.5, 5, 7.5, and 10%) membranes. Reproduced from [130], with permission from Elsevier, 2020.

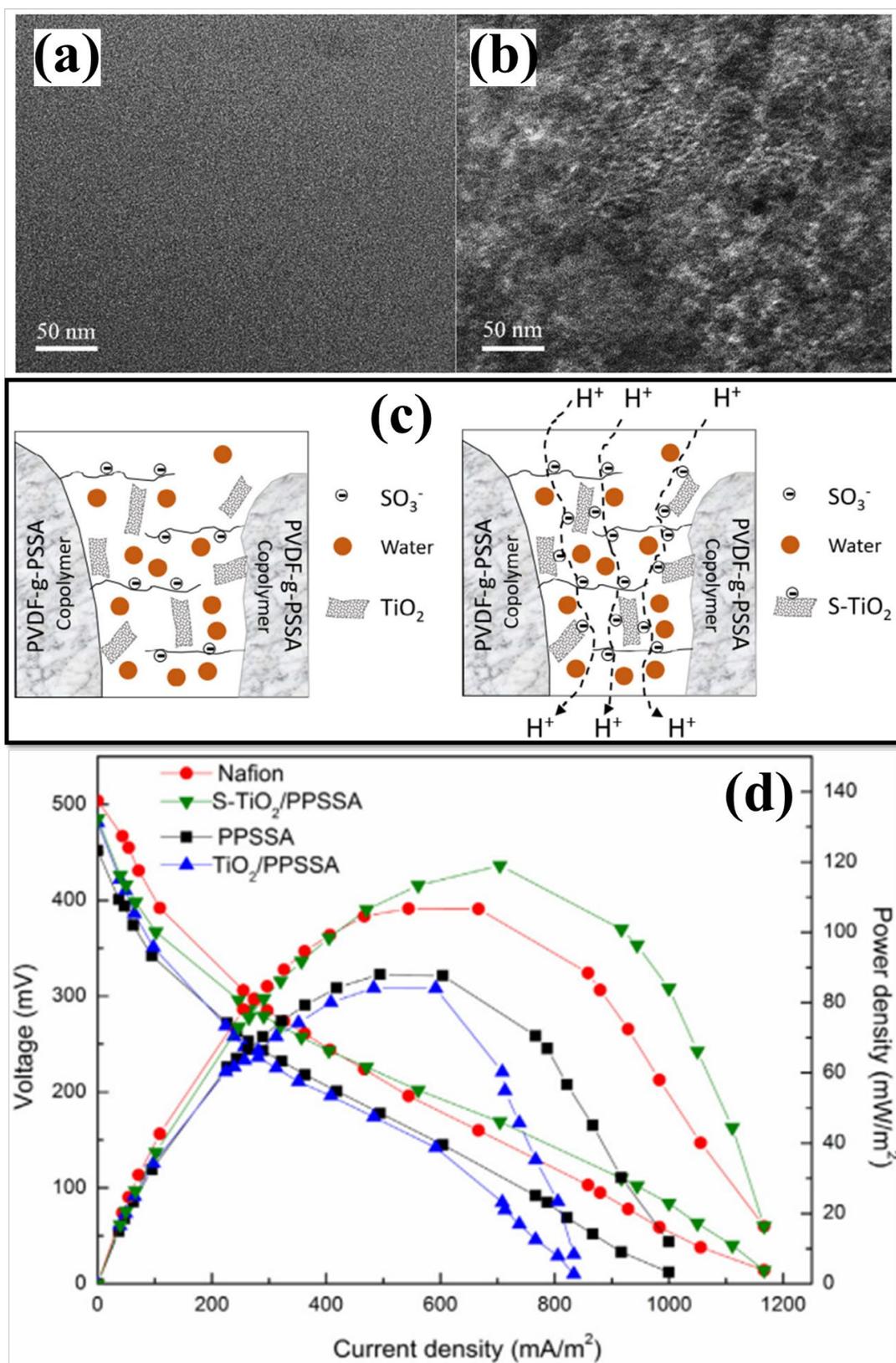


Figure 4. Transmission electron microscope images of (a) PPSSA and (b) PPSSA-sTiO₂ membranes. (c) Diagrammatic representation of the PPSSA-sTiO₂ membranes' proton transport routes. (d) Polarization and power density curves of Nafion, PPSSA, PPSSA-TiO₂, and PPSSA-sTiO₂ membranes. Reproduced from [139], with permission from Elsevier, 2019.

4. Sulfonated Graphene Oxide Containing Polymer Membrane for MFC Applications

The two-dimensional structure of graphene oxide (GO) is used as an inorganic filler during composite membrane fabrication for its excellent physicochemical characteristics, such as high hydrophilicity, PC, more surface area, and tremendous mechanical strength [140–142]. The presence of different oxygen functional groups (i.e., hydroxyl, carboxylic, and epoxy groups) in GO is responsible for its enhanced hydrophilicity. The rigid mechanical strength of GO is also due to the strong covalent bonds in its hydrophobic region [140,142]. As discussed, the SPEEK polymer exhibits immense PEM properties, such as excellent thermal, mechanical, chemical stability, hydrophilicity, and low cost with high ionic conductivity. In this view, Leong et al. successfully fabricated a GO/SPEEK composite PEM with self-synthesized GO as a nanofiller [140]. GO/SPEEK composite membranes are enhanced for transferring protons through the Grotthuss mechanism by a hydrogen bonding network that increases the composite membrane PC. Thus, the GO-SPEEK composite membrane exhibits enhanced physicochemical properties with improved PC ($1.48 \times 10^{-3} \text{ S cm}^{-1}$) and oxygen diffusion coefficient ($1.154 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The performance of MFCs with GO-SPEEK composite membrane exhibited a higher CE (16.88%) than Nafion 117 (12.31%) and was recommended as a promising alternative to Nafion 117 membrane in MFCs [140]. A similar kind of composite PEM was developed by Shabani et al. by introducing nano-sized GO into SPEEK for generating electricity while simultaneously treating wastewater [143]. In MFCs, the SPEEK-GO composite membrane outperformed the commercial Nafion 117 membrane in terms of WU, PD (53.12 mW m^{-2}), and CE (3.74 0.18%), as well as COD removal efficiency (88.71 0.29%) [143]. In another approach, GO-SPEEK and Silver-GO/GO/SPEEK (AgGO-GO-SPEEK) self-fabricated composite membranes were developed and used in MFC applications for their higher PC, reduced oxygen crossover, and good antibiofouling properties [144]. The inclusion of Ag NPs inhibits microbial growth in the membrane. The AgGO-GO-SPEEK membrane had a 54.2% higher PC and a 76.7% lower oxygen diffusion coefficient than the commercial Nafion 117 membrane. Furthermore, the AgGO-GO-SPEEK composite membrane demonstrated low internal resistance with improved PD during MFC operation and outperformed the commercial Nafion 117 membrane [144]. Along with SPEEK polymer, other sulfonated hydrocarbon polymers (e.g., sulfonated polyethersulfone (SPES), sulfonated polysulfone) have sparked interest in composite PEMs. Ali et al. developed a GO-incorporated SPES composite membrane (GO/SPES) in MFCs for simultaneous electricity generation and wastewater treatment [145]. The prepared GO-SPES composite membrane exhibited a higher PD of 101.2 mW m^{-2} and a current density of 613 mA m^{-2} with an 80% COD removal efficiency [145]. Inexpensive and high-availability PVA with higher thermal and chemical stability was also introduced as a polymer matrix for developing PEM. Introducing the inorganic fillers into the PVA polymer matrix enhances its PC property and tunes its physical and electrochemical properties to be suitable for IEM. GO, an inorganic filler, was impregnated into a PVA and silicotungstic acid (STA) matrix for developing a low-cost PVA/STA/GO composite membrane by solution casting technique for generating electricity using SCMFCs [146]. The GO incorporation in the composite membrane enhances its PC and antibiofouling properties. Moreover, SCMFCs with a PVA/STA/GO composite membrane generated a maximum PD of 1.9 W m^{-3} by treating acetate wastewater with 91% substrate removal efficiency [146]. Likewise, Rudra et al. prepared a graphite-oxide-based nanocomposite membrane for harvesting electricity from SCMFCs containing crosslinked PVA and sulfonated styrene (SS) (polymerized in situ) as the backbone matrix [147]. The WU, swelling behavior, and oxygen diffusivity of the composite membrane have been reduced due to the hydrogen bonding of graphite oxide to the substrate. Thus, the composite membrane with 0.4% graphite oxide in SCMFCs exhibited a higher PD of 193.6 mW m^{-2} with 803.33 mA m^{-2} current density and ~81.89% COD removal efficiency [147].

Recently, novel PEM has been developed by incorporating GO nanofiller into PVDF and cellulose acetate (CA) polymer blend and used in MFCs for generating clean energy [148]. The presence of CA in this composite membrane has improved its ability to stop

biofouling, the conductivity of protons, porosity, and the ability to attract water. In the same way, the thermal and chemical stability of the composite membrane was attributed to PVDF and GO for improving surface area along with membrane hydrophilicity [148]. This study was extended by the same group, in which superior low-cost PEM was developed, consisting of PVDF, CA, and reduced GO (rGO) for extracting electricity using MFCs [137]. During MFC performances, it was seen that the performance of the composite membrane was similar to that of commercial membranes. It has been seen that composite membranes generated a higher COD removal efficiency ($92.0 \pm 0.8\%$) along with 118 mW m^{-2} of PD [137]. Despite developing composite PEM using a synthetic polymer matrix, Holder et al. utilized biopolymers such as chitosan (CS), in which GO was introduced as a filler to form CS/GO composite membrane [149]. In addition, CS/GO cross-linked with sulfuric acid or phosphoric acid for developing CS/GO-P and CS/GO-S composite membranes. During MFC operation using wastewater, CS/GO-P-membrane-equipped MFCs generated maximum PD (16.35 mW m^{-3}) and COD removal efficiency (89.52%). In the same conditions, the CS/GO-S delivered a PD of 6.94 mW m^{-3} and COD removal efficiency of 31.99% [149].

Because of a reasonable amount of oxygen-containing functional groups (e.g., hydroxyl, carboxyl, and $-\text{SO}_3\text{H}$ groups), sulfonated GO (sGO) can effectively increase the PC, mechanical stability, and antifouling properties in the hybrid composite membrane when compared to GO [150–152]. The phosphoric-acid-doped PBI can also be used as a base polymer matrix for its excellent chemical, thermal, and mechanical properties to develop composite membranes for MFC applications [89,150,153]. The PC depends on an acid-doped membrane's acid doping level (ADL). However, increasing the ADL in the membrane reduces its mechanical strength. Hence, modifications such as incorporating inorganic nanofillers have been performed to develop PBI nanocomposite with enhanced mechanical and thermal stability and dimensional stability. In this way, Mondal et al. fabricated sulfonated SPBI-based composite PEM by introducing different proportions of SGO (Figure 5a) [150]. For sulfonating PBI polymers, it reacts with 2-chloro ethane sulfonic acid, in which the PBI imidazole nitrogen atom has been covalently grafted with alkyl sulfonic acid. The GO nanofiller was synthesized using a modified Hummers' method and sulfonated with chlorosulfonic acid. Figure 5b shows that SPBI-5% SGO exhibited a higher PC of 0.018 S cm^{-1} than pristine PBI membrane ($4.28 \times 10^{-4} \text{ S cm}^{-1}$). This increment was attributed to the development of more proton transport channels through H-bonding developed by a higher content of $-\text{SO}_3\text{H}$ groups in the PBI matrix during SGO inorganic filler incorporation. During the MFC operation (Figure 5c), it was observed that the homogenous and widespread distribution of SGO in the 3% SPBI-SGO composite membrane exhibited a higher OCV of $\sim 669 \pm 18 \text{ mV}$ and a maximum current density of $2019.06 \text{ mA m}^{-2}$ at 0.234 V. It was expected that MFCs with a 5% SPBI-SGO composite membrane would exhibit a higher OCV and current density due to its enhanced PC and IEC values. However, it performed worse than the 3% SPBI-SGO composite membrane, owing to a higher concentration of SGO agglomerate on the PBI surface and more sulfonic acid groups on the membrane surface. Therefore, the substrate-generated cations interacted with those groups enhancing membrane resistivity. It was also noted that the maximum PD of 472.46 mW m^{-2} was generated by MFCs equipped with 3% SPBI-SGO than pristine PBI, SPBI, or other composite membranes. Hence, MFCs with a 3% SPBI-SGO composite membrane exhibited increased current generation with reduced voltage drops, recommended as an alternative PEM candidate for MFC application [150]. Moreover, Shabani et al. prepared a cost-effective sulfonated polyethersulfone (SPES)-based hybrid composite membrane by introducing GO, thiolated GO (TGO), and SGO filler for enhancing MFC performances [154]. The proton selectivity of the composite membrane was improved by introducing $-\text{SO}_3\text{H}$ and sulfhydryl ($-\text{SH}$) groups in the fillers. From this, the 1.8% SPES-SGO composite membrane exhibited higher proton (H^+) selectivity than other cations (Li^+ , N^+ , and K^+). Hence, the functionalized GO nanocomposite membranes in MFCs showed higher PD and CE with higher COD removal efficiency [154]. A novel composite antibiofouling PEM has been developed with the introduction of SGO into the

PVDF-g-PSSA polymer matrix, and its MFC performance was evaluated [151]. The SO_3^- groups in the composite PVDF-g-PSSA/SGO membrane increase the WU, hydrophilicity, and ionic conductivity of the membrane, which enhances the electricity generation during MFC operation [151]. In another way, the same research group made new PVDF-g-PSSA-based composite membranes with SiO_2 -filled SGO nanofillers (Figure 6a) to improve the PC and antibiofouling properties [155]. SiO_2 has been inserted into SGO through in situ hydrolysis, with ethyl orthosilicate used as a precursor to obtain SiO_2 /SGO. Furthermore, the various concentrations of developed SiO_2 /SGO NPs (0.1, 0.5, 1.0, and 2.0%) are prepared and added to the PVDF-g-PSSA polymer matrix. Increasing the $-\text{SO}_3\text{H}$ content of the membrane improves PC, as seen in the impedance spectra in Figure 6b. Incorporating SiO_2 /SGO enhances the proton transport channels for migration and increases the composite membrane's hydrophilic properties (WU%). These improvements improved the composite membrane's PC, which was higher at 1% SiO_2 /SGO. Further increasing the SiO_2 /SGO NP content decreases the composite membrane's PC values through the particle agglomeration that prevents the polymer chain from free movement and thus reduces the proton transport. MFCs with PVDF-g-PSSA/SGO/ SiO_2 membrane outperformed MFCs in terms of PD and current density (185 mW m^{-2} and 1338 mA m^{-2} , respectively) as shown in Figure 6c. In addition, low resistance and reduced membrane fouling result in 75% COD removal efficiency (Figure 6d,e) [155]. The physicochemical properties and performance evaluation results of sulfonated GO-incorporated polymer membranes for MFC applications have been provided in Table 3.

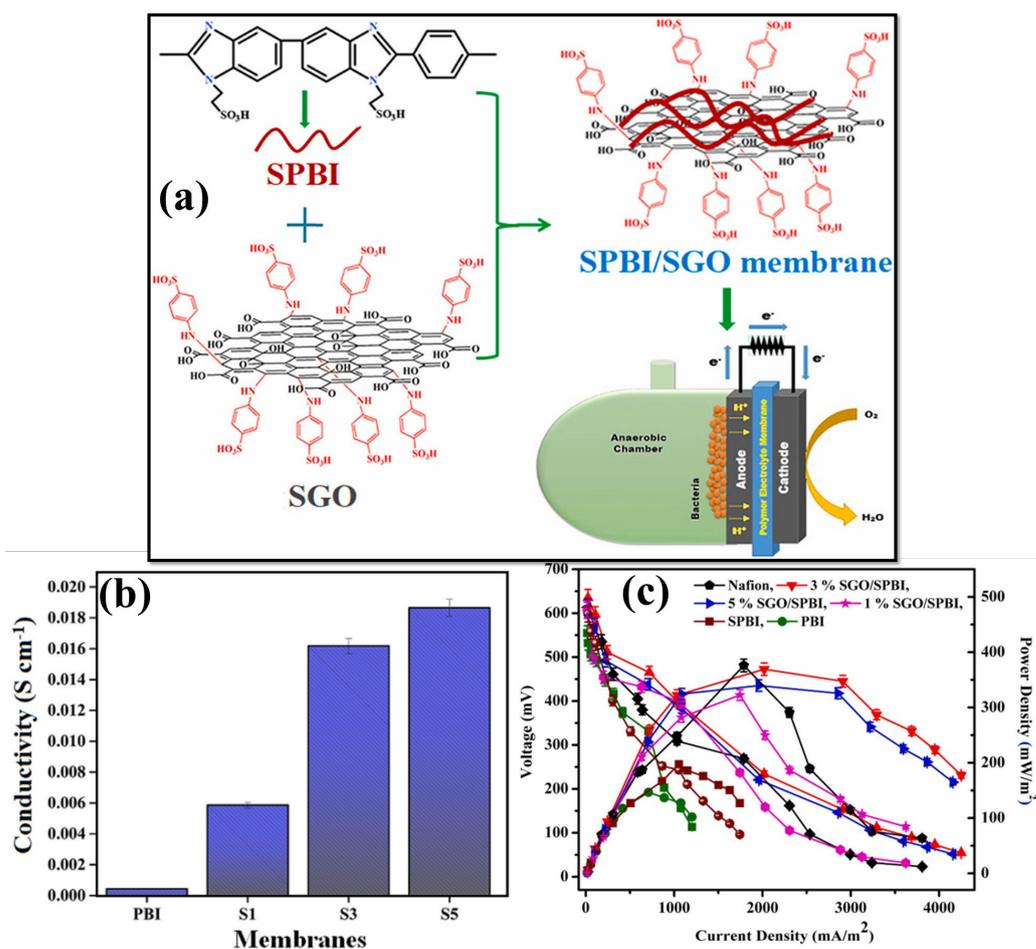


Figure 5. (a) A schematic representation of SPBI-SGO membrane preparation progression for MFC system. (b) Proton conductivity and (c) MFC performances of PBI, SPBI, and different concentrations of SGO (1, 3, and 5%) in the SPBI membrane. Reproduced from [150], with permission from Elsevier, 2020.

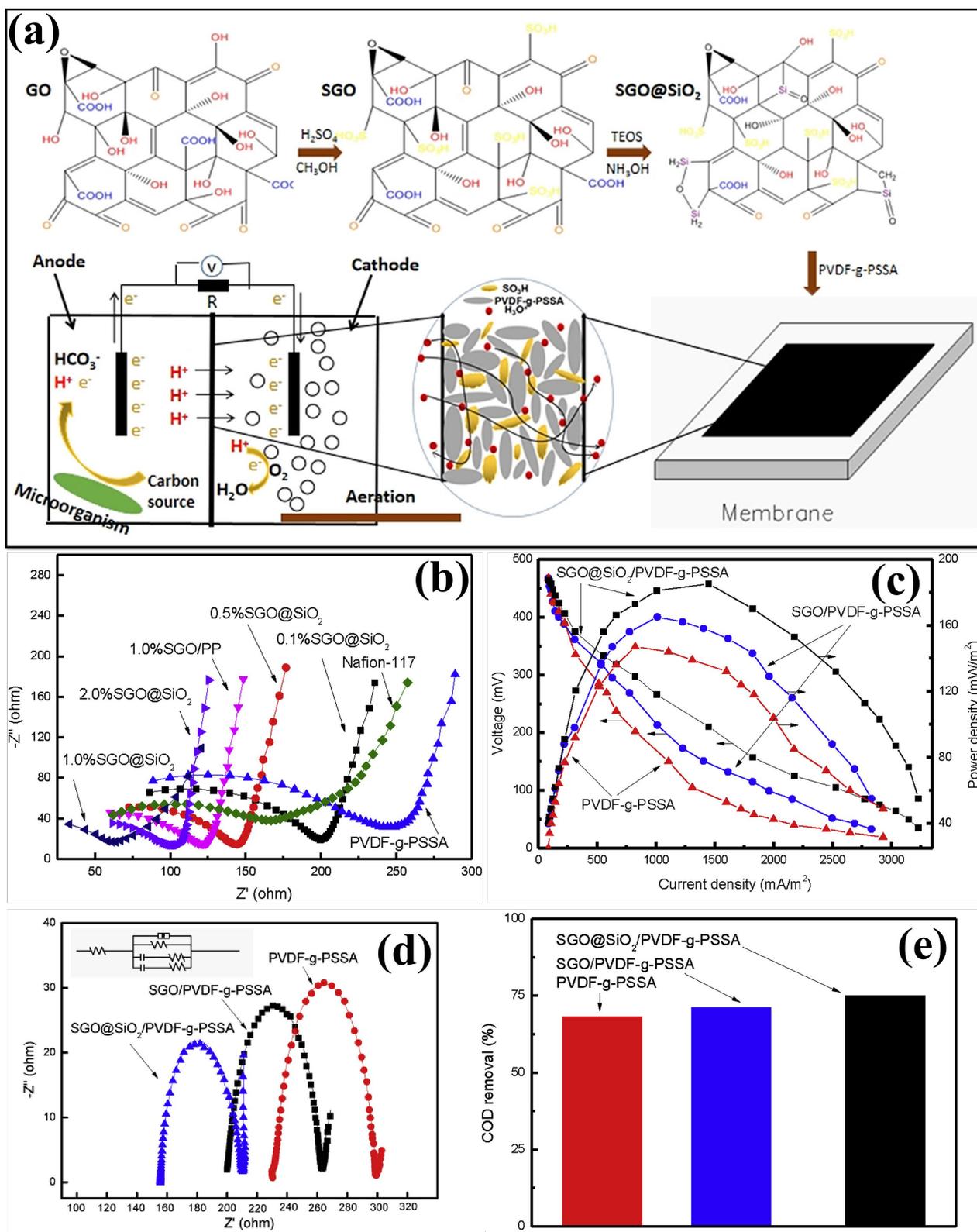


Figure 6. (a) A schematic representation of SGO@SiO₂ preparation steps and PVDF-g-PSSA/SGO@SiO₂ membrane developments for MFC device. (b) EIS performance of Nafion 117, PVDF-g-PSSA, and different ratios of PVDF-g-PSSA/SGO@SiO₂ membranes. (c) Polarization curves, (d) EIS, and (e) COD removal of PVDF-g-PSSA, PVDF-g-PSSA/SGO and PVDF-g-PSSA/SGO@SiO₂ membranes. Reproduced from [155], with permission from Elsevier, 2019.

Table 3. Physicochemical properties and performance evaluation results of sulfonated graphene oxide containing polymer membrane for MFC applications.

IA	Polymer	WU (%)	IEC (meqg ⁻¹)	PC (S/cm)	OCV (mV)	IR (Ω)	CD (mA m ⁻²)	PD (mW m ⁻²)	CE (%)	COD (%)	Ref.
	Nafion				~716 ± 21			481.3			
	PBI			4.28 × 10 ⁻⁴	~477 ± 13		709.19				
SGO-1%	SPBI				~567 ± 16						[150]
SGO-3%	SPBI		0.912		~669 ± 18		2019.06	472.46			
SGO-5%	SPBI	21	1.001	0.018	~625 ± 18		1959.43				
	Nafion	17.5	0.86 ± 0.1	0.0013			233.3 ± 3	35.9 ± 2	2.28 ± 0.2	82.71 ± 5	
	PES	5.41	0.28 ± 0.1	0.00021							
	SPES	12.33	0.36 ± 0.1	0.00032			216.7 ± 3	27.8 ± 2	2.19 ± 0.2	79.76 ± 5	
GO-0.6%	SPES	20.71	0.42 ± 0.1	0.00044			218.7 ± 7	28.5 ± 2	2.04 ± 0.2	75.2 ± 5	
GO-1.2%	SPES	22	0.54 ± 0.1	0.00052			222.1 ± 3	32.1 ± 2	2.20 ± 0.2	80.74 ± 5	
GO-1.8%	SPES	23.13	0.74 ± 0.1	0.00056			225 ± 3±3	39.2 ± 2	2.28 ± 0.2	86.47 ± 5	
SGO-0.6%	SPES	28.41	0.61 ± 0.1	0.00105			233.5 ± 3	46.8 ± 2	2.13 ± 0.2	78.21 ± 5	[154]
SGO-1.2%	SPES	33.54	0.72 ± 0.1	0.00125			276.4 ± 3	61.5 ± 2	2.64 ± 0.2	85.41 ± 5	
SGO-1.8%	SPES	36.32	0.84 ± 0.1	0.00142			300 ± 3	66.4 ± 2	3.73 ± 0.2	89.85 ± 5	
TGO-0.6%	SPES	24.55	0.55 ± 0.1	0.00084			223.6 ± 3	43.4 ± 2	2.18 ± 0.2	72.53 ± 5	
TGO-1.2%	SPES	26.22	0.63 ± 0.1	0.00101			255 ± 3	51.7 ± 2	2.51 ± 0.2	85.22 ± 5	
TGO-1.8%	SPES	30	0.77 ± 0.1	0.00125			275 ± 3	54.13 ± 2	3.20 ± 0.2	88.07 ± 5	
	PVDF-g-PSSA	25.00	0.58	0.046		243.9		106.67			
GO-1.0%	PVDF-g-PSSA	29.32	0.79	0.065		189.		138.02			
SGO-0.1%	PVDF-g-PSSA	26.45	0.64	0.056							
SGO-0.5%	PVDF-g-PSSA	30.14	0.81	0.068							
SGO-1.0%	PVDF-g-PSSA	32.56	1.24	0.083		167.9		180.27			[151]
SGO-1.5%	PVDF-g-PSSA	33.05	1.08	0.079							
SGO-2.0%	PVDF-g-PSSA	34.24	0.85	0.070							
	Nafion	20.00	0.89	0.078		210.5		132.02			
	Nafion	20.1 ± 0.1	1.0 ± 0.1	0.071 ± 0.003		210		132		74	
	PVDF-g-PSSA	25.0 ± 0.2	0.60 ± 0.2	0.046 ± 0.003		228		147		68	
SGO-1.0%	PP	32.4 ± 0.2	1.4 ± 0.2	0.073 ± 0.002		191		166		71	
SGO@SiO ₂ -0.1%	PVDF-g-PSSA	26.1 ± 0.3	1.0 ± 0.2	0.068 ± 0.002							[155]
SGO@SiO ₂ -0.5%	PVDF-g-PSSA	30.1 ± 0.1	1.2 ± 0.2	0.072 ± 0.004							
SGO@SiO ₂ -1.0%	PVDF-g-PSSA	34.2 ± 0.2	1.6 ± 0.1	0.078 ± 0.004		152	1338	185		75	
SGO@SiO ₂ -2.0%	PVDF-g-PSSA	33.6 ± 0.2	1.4 ± 0.2	0.074 ± 0.003							

IA—inorganic additives, WU—water uptake, IEC—ion exchange capacity, PC—proton conductivity, OCV—open circuit voltage, IR—internal resistance, CD—current density, PD—power density, CE—coulombic efficiency.

5. Sulfonated Fe₃O₄ Containing Polymer Membrane for MFC Applications

Developing hybrid membranes with Fe₃O₄ and its modified version for various systems was intriguing [156–158]. In this connection, Prabhu and Sangeetha prepared the composite SPEEK-Fe₃O₄ by incorporating different weight percentages (2.5, 5.0, 7.5, and 10%) of Fe₃O₄ into the SPEEK polymer matrix [159]. The effect of Fe₃O₄ on the composite membrane was measured in terms of its electrochemical performance, ability to take in water, ability to let oxygen pass through it, and ability to conduct ions. The 7.5% Fe₃O₄-SPEEK composite membrane fabricated MFCs exhibited a lower oxygen diffusion rate with increased PC and attained a maximum PD of 104 mW m⁻² [159]. Solution casting techniques are commonly preferred for developing polymer nanocomposite membranes because of their efficiency and applicability, even in smaller quantities [81,160]. However, this technique is unsuitable during large-scale membrane development for its innate inappropriateness over commercial standards. Palma et al. fabricated a polyethersulfone (PES)-based nanocomposite membrane using different contents of Fe₃O₄ NPs using melt extrusion membrane for developing the membrane on a large scale [81]. The composite

membrane performance was evaluated using H-type MFC with sodium-acetate-containing synthetic wastewater. Incorporating Fe_3O_4 NPs into the membrane increases its mechanical strength, which is desirable for long-term stable MFC operation. During MFC operation, the highest PD of $9.59 \pm 1.18 \text{ mW m}^{-2}$ and current density of $38.38 \pm 4.73 \text{ mA m}^{-2}$ for composite membrane with 20% Fe_3O_4 NPs incorporation were reported [81]. In a second study, they looked at how pretreating PES/ Fe_3O_4 nanocomposite membranes affected the electrochemical performance of MFCs [161]. It was observed that pretreating the membrane involved boiling the composite membrane for 1 h in deionized water and immersing it in H_2SO_4 (0.5 M) for 1 h. As a result, PES- Fe_3O_4 (10 wt%) composite membrane exhibited a membrane resistance of $7.55 \text{ k}\Omega$ with a PD of $10.59 \pm 0.72 \text{ mW m}^{-2}$ and a current density of $52.07 \pm 0.86 \text{ mA m}^{-2}$. Hence, the pretreatment method reduces the incorporation of the NPs used effectively for MFC applications [161]. In another approach, permanently modified magnetite NPs filler (Fe_3O_4) has been achieved through the direct degree of sulfonation using various amounts of sulfuric acid (0.5, 1, and 1.5 M) [162]. The micro- and crystalline nature of the magnetite NPs structure was not altered during the sulfonation process, as confirmed by experimental analysis. Then, the composite PES-based membrane was fabricated by introducing various contents of sFe_3O_4 (5, 10, 15, and 20 wt%), and their performance was evaluated in H-type MFC using an acetate substrate. Here, the large number of $-\text{SO}_3\text{H}$ and $-\text{OH}$ functional groups enhances the membrane hydrophilicity, which improved the WU, IEC, and PC values with reduced oxygen diffusion properties of the sulfonated membranes. The absorption peaks for pristine Fe_3O_4 and sulfonated Fe_3O_4 NPs were analyzed through the FTIR technique and shown in Figure 7, which is used to confirm the sulfonation functional group. During 350 h of MFC operation, the MFC coupled with the PES20_S composite membrane exhibited the highest total organic carbon (TOC) removal rate of 82.74% (Figure 7). It was observed that the PES10_S composite membrane showed the highest power and current densities of 270% and 117% higher than the Nafion 117 membrane, respectively, along with 868.09 mV of OCV and 29.58% of CE [162]. The physicochemical properties and performance evaluation results of sulfonated Fe_3O_4 incorporated polymer membranes for MFC applications have been provided in Table 4.

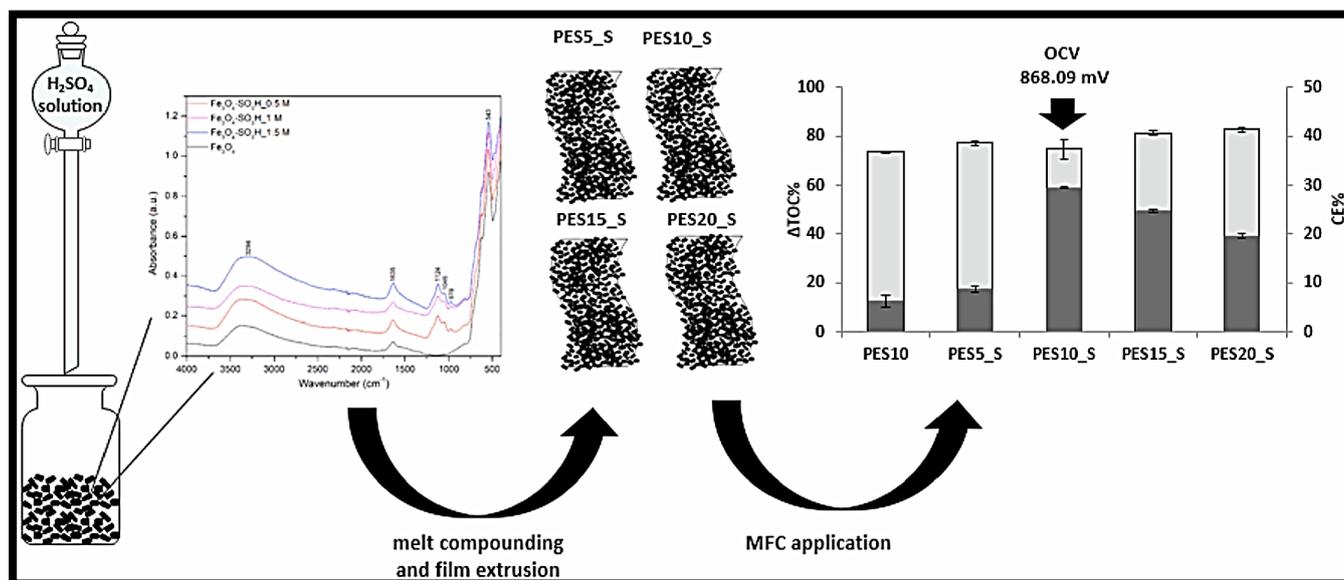


Figure 7. The overall process (FT-IR spectra of Fe_3O_4 and sFe_3O_4) and performances (coulombic efficiency (grey) and total organic carbon removal) of sulfonated Fe_3O_4 /PES nanocomposite membranes. Reproduced from [162], with permission from Elsevier, 2020.

Table 4. Physicochemical properties and performance evaluation results of different kinds of sulfonated additives containing polymer membrane for MFC applications.

IA	Polymer	WU (%)	IEC (meqg ⁻¹)	PC (S/cm)	K0 (cms ⁻¹)	OCV (mv)	IR (Ω)	CD (mA m ⁻²)	PD (mW m ⁻²)	Ref.
Fe ₃ O ₄ -10%	PES	1.56 ± 0.24	0.07 ± 0.02		1.26 × 10 ⁻³	550.50 ± 3.53	13.87 ± 1.79	20.78 ± 0.30	5.72 ± 0.81	
SFe ₃ O ₄ -5%	PES	1.99 ± 0.04	2.08 ± 0.19		1.10 × 10 ⁻⁴	580.90 ± 32.4	7.92 ± 0.75	47.96 ± 3.58	18.70 ± 0.48	
SFe ₃ O ₄ -10%	PES	3.78 ± 0.20	5.49 ± 0.43		1.28 × 10 ⁻⁴	150.67 ± 8.45	5.77 ± 0.96	150.67 ± 8.4	65.24 ± 5.79	[162]
SFe ₃ O ₄ -15%	PES	3.98 ± 0.01	6.49 ± 0.19		1.45 × 10 ⁻⁴	132.84 ± 4.29	5.42 ± 0.25	132.84 ± 4.2	47.82 ± 4.32	
SFe ₃ O ₄ -20%	PES	5.23 ± 0.30	9.76 ± 0.52		1.46 × 10 ⁻⁴	104.91 ± 5.62	5.91 ± 0.33	104.91 ± 5.6	32.52 ± 3.34	
	SPSEBS	37.9	1.9	0.98 × 10 ⁻²	2.2 × 10 ⁻⁶		42			
SPOSS-2%	SPSEBS	38.2	2.6	1.2 × 10 ⁻²	1.7 × 10 ⁻⁶		38			
SPOSS-4%	SPSEBS	39.9	2.9	1.36 × 10 ⁻²	1.9 × 10 ⁻⁶		36			
SPOSS-6%	SPSEBS	41	3.7	1.40 × 10 ⁻²	1.6 × 10 ⁻⁶		31		126	[163]
SPOSS-8%	SPSEBS	39.4	2.9	1.3 × 10 ⁻²	1.9 × 10 ⁻⁶		35			
	Nafion	22	1.2	0.77 × 10 ⁻²	2.4 × 10 ⁻⁶		45			
	SPEEK	29 ± 0.05	1.4 ± 0.3	0.92 × 10 ⁻²	2.1 × 10 ⁻⁶		37		100 ± 1.2	
S-POSS-2.5%	SPEEK	33.8 ± 0.03	1.5 ± 0.06	1.25 × 10 ⁻²	1.65 × 10 ⁻⁶		31			
S-POSS-5%	SPEEK	35.5 ± 0.08	1.8 ± 0.05	1.31 × 10 ⁻²	1.42 × 10 ⁻⁶		28		162 ± 1.4	[164]
S-POSS-7.5%	SPEEK	34.6 ± 0.07	1.7 ± 0.02	1.12 × 10 ⁻²	1.69 × 10 ⁻⁶		33			
S-POSS-10%	SPEEK	32.4 ± 0.02	1.6 ± 0.07	1.02 × 10 ⁻²	1.82 × 10 ⁻⁶		35			
	Nafion	22 ± 0.03	1.2 ± 0.05	0.81 × 10 ⁻²	2.4 × 10 ⁻⁶		40		154 ± 1.7	
	SPEES	29.8 ± 0.3	1.4 ± 0.05	1.12 × 10 ⁻²	1.9 × 10 ⁻⁶		36		75	
ZnO-7.5%	SPEES	30.5 ± 0.2	1.3 ± 0.05	1.19 × 10 ⁻²	1.83 × 10 ⁻⁶		34			
S-ZnO NR-2.5%	SPEES	32.5 ± 0.2	1.6 ± 0.03	1.29 × 10 ⁻²	1.71 × 10 ⁻⁶		32			
S-ZnO NR-5%	SPEES	33.7 ± 0.5	1.8 ± 0.07	1.36 × 10 ⁻²	1.67 × 10 ⁻⁶		30			[165]
S-ZnO NR-7.5%	SPEES	34.6 ± 0.6	2.0 ± 0.05	1.4 × 10 ⁻²	1.51 × 10 ⁻⁶		29		142	
S-ZnO NR-10%	SPEES	31.8 ± 0.9	1.9 ± 0.04	1.21 × 10 ⁻²	2.45 × 10 ⁻⁶		34			
	Nafion	22 ± 0.5	1.2 ± 0.06	0.81 × 10 ⁻²			40		130	
6% SZnO NR	SPSEBS				1.49 × 10 ⁻²				147	[166]

IA—inorganic additives, WU—water uptake, IEC—ion exchange capacity, PC—proton conductivity, K0—oxygen mass transfer coefficient, OCV—open circuit voltage, IR—internal resistance, CD—current density, PD—power density.

6. Different Kinds of Sulfonated Additives in Polymer Membrane for MFC Applications

The outstanding chemical stability, conductivity, and antimicrobial property of silver (Ag) were also investigated for its application as an inorganic filler in fabricating composite PEM for MFC applications [144,167–169]. The antimicrobial activity of Ag not only reduces the biofilm formation in the membrane but also reduces the microbial growth responsible for generating electrons [167,170,171]. Thus, the optimizing Ag NPs concentration as fillers in composite membrane preparation is necessary. Kugarajah and Dharmalingam fabricated a SPEEK-Ag composite membrane by incorporating different concentrations of Ag into the SPEEK polymer matrix and studying their effect on MFC performance and the microbial community [167]. During MFC operation, a maximum PD of 156 ± 0.5 mW m⁻² was achieved for SPEEK-7.5 wt% Ag than other composite membranes or Nafion 117. Furthermore, the antibiofouling effect of Ag in composite membranes contributed to its long-term operation and improved MFC performance [167]. Tiwari et al. utilized cost-effective borosilicate glass as a backbone matrix incorporated with PVA/Nafion for casting a PVA/Nafion/borosilicate composite (MPN) membrane for MFC applications [172]. It was observed that MFCs with MPN membrane generated a higher PD (6.8 W m⁻³) than Nafion 117 membrane (7.1 W m⁻³). Hence, the low-cost MPN membranes are an alternative to the Nafion 117 membrane in real-time MFC applications [172]. Apart from inorganic fillers, heteropoly acids (HPAs) such as silico tungstic acids (STAs) with high protonic conductivity range (2 × 10⁻² S cm⁻¹) have also been used as fillers in polymer matrix for improving the

stabilities and PC [173]. The hybrid composite membrane was fabricated by entrapping STA particles in the SPEEK membrane for SCMFC applications. The SPEEK-7.5% STA composite membrane exhibited a high power density (207 mW m^{-2}) than Nafion 117 during SCMFC operation [173]. Similarly, phosphotungstic acid (PWA) and sulfonated polystyrene (SPS) have been introduced into the SPEEK polymer matrix to create more proton pathways for enhanced PC in a developed composite PEM for MFC applications [174]. Saniei et al. created hydrophilic goethite NPs and their derivatives, goethite–tannic acid–sulfanilic acid NPs, and goethite–tannic acid NPs [175]. The composite SPEEK membrane has been fabricated by embedding the as-prepared NPs into the SPEEK polymer matrix and is used as a membrane in MFC operations. SPEEK with 0.5 wt% of goethite exhibited higher PD (73.7 mW m^{-2}), current density (293 mA m^{-2}), and CE (52.6%) with increased COD removal efficiency (97.6%) [175]. Recently, Sugumar and Dharmalingam prepared a new PEM by solution-casting sulfonated polyhedral oligomeric silica (S-POSS) into the SPSEBS base polymer matrix to improve mechanical strength and PC [163]. They also statistically optimized (RSM) various pH, substrate concentrations, and anode materials with SPSEBS/6%-SPOS composite membranes for generating electricity through tubular MFCs. It has been observed that maximum PD (126 mW m^{-2}) was obtained at 75% substrate concentration, maintaining the pH 7 with graphite rod as anode material in MFCs operating over 3 weeks [163]. The same research group took a different approach, incorporating S-POSS into the SPEEK polymer matrix to create a promising PEM candidate for improving tubular MFC stability and performance [164]. The inorganic S-POSS filler created more ion transport channels in the composite membrane with its hydroxide ions. This made the PC and WU go up. Along with this, they observed that bacterial strains such as *Firmicutes* were, *Gammaproteobacteria*, and *Betaproteobacteria* identified as bioelectrogenesis and provided the future view on different electron transfer mechanisms [164]. The physicochemical properties and performance evaluation results of various sulfonated additives incorporated in polymer membranes for MFC applications have been provided in Table 4.

In some instances, zinc oxide (ZnO) is used in anode or cathode catalysts for enhancing antibiofouling properties by suppressing the formation of biofilms [165,176,177]. In the case of membrane applications as nanofillers, ZnO NPs are converted into nanorods (ZnO NR) to increase the surface area for enhancing the WU property [165]. If ZnO NR fillers were used in the composite membrane, the ionic conductivity was attributed solely to the vehicular mechanism (via water). As a result, sulfonation of ZnO NR (S-ZnO NR) is performed in addition to the vehicular mechanism to increase PC via Grotthuss mechanism (via SO_3H groups), as shown in Figure 8d. As a result, the researchers incorporated different sulfonated ZnO NR (hydrothermally synthesized) ratios (2.5, 5, 7.5, and 10%) into a sulfonated poly(phenylene ether ether sulfone) (SPEES) polymer for fabricating SPEES/SZnO NR composite membranes in tubular MFCs. At this point, the SPEES polymer and ZnO NR filler enhance the membrane's hydrophilic properties, improving its water holding, IEC, and PC. Both vehicular (through water) and Grotthuss mechanism (through $-\text{SO}_3\text{H}$) means of proton transport have been observed in SPEES/SZnO NR composite membranes, due to the presence of nanorod structure (improving WU property) and the sulfonic acid group. In this case, ionic transport is also aided by SO_3^- domains that exhibit strong electrostatic attraction, with the $-\text{SO}_3\text{H}$ group interacting directly with the polymer structure (Figure 8d). In addition, S-ZnO NR incorporation also improves the composite membrane's mechanical stability and antibiofouling property. At the start of an MFC operation, the voltage output goes down because the uptake of microorganisms means the medium needs to be filled with new material. It was observed (Figure 8c) that MFCs equipped with SPEES/7.5% SZnO NR delivered a maximum PD of $142 \pm 1.2 \text{ mW m}^{-2}$ with lower internal resistance and was recommended to be used as PEM in MFCs for a long time of operation [165]. In a different approach, the same research group incorporated SZnO into SPSEBS polymer to prepare PEM, which was then used in MFCs for the green electricity generation [166]. Here, SZnO NR was used to improve the proton transport mechanisms and make the proton transport more conductive. This made the surface area bigger and the

material more water-friendly. The highest PC of $1.49 \times 10^{-2} \text{ S cm}^{-1}$ has been observed for the SPSEBS/6% SZnO composite membrane [166]. Thus, it has been confirmed that the homogeneous addition of inorganic additives to the polymer matrix effectively improved the overall physicochemical properties, stabilities, and MFC performances.

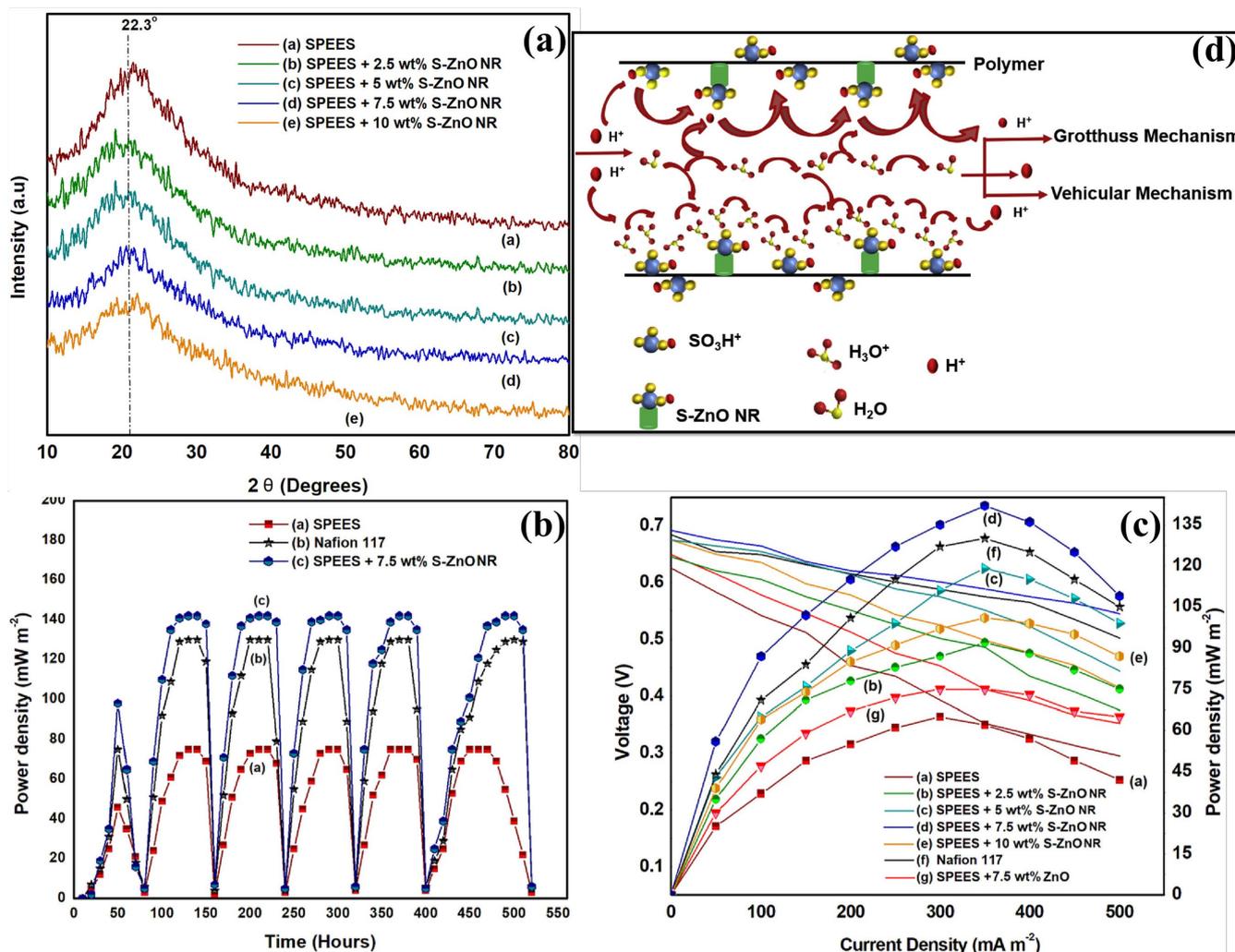


Figure 8. (a) XRD spectra of SPEES and different concentrations of sZnO NR (2.5, 5, 7.5, and 10%). MFC performances of (b) power density vs. time and (c) voltage vs. current density. (d) A graphic illustration of the ion transport mechanism in SPEES-sZnO NR composite membrane. Reproduced from [165], with permission from Elsevier, 2021.

7. Concluding Remarks

Recently, global researchers have raised significant concerns for the energy and environmental research and development sectors. In this case, energy generation and water remediation are urgently important categories to address for a safer human life. Among the various devices, the MFC can produce bioenergy by cleaning wastewater. Thus, considerable attention has been provided to the MFC system. Usually, the MFC's performance depends on components and process variables. The proton exchange membrane is the most important candidate for making the MFC work best by controlling the substrate/oxygen crossover and improving proton transport. There are different kinds of commercial membranes available for MFC applications. However, commercial membranes have certain disadvantages, such as high cost and fuel crossover. To overcome these issues in the polymer membrane, different kinds of inorganic additives have been included homogeneously. The inclusion of inorganic additives has significantly improved the membrane properties

and performance. This review details the impact of sulfonated inorganic additives on their functional group surface properties and the base polymer material. Sulfonated inorganic additives, such as sulfonated silica (S-SiO₂), sulfonated titania (S-TiO₂), sulfonated graphene oxide (S-GO), sulfonated iron oxide (S-Fe₃O₄), and sulfonated zinc oxide (S-ZnO), have effectively altered the overall physicochemical properties of the membrane. Furthermore, the surface morphology of the inorganic additive (such as nanoparticles, nanotubes, 2D nanosheets, and core@shell) plays an important role in the membrane for controlling the oxygen crossover. The sulfonic acid functional group enhances the hydrophilicity of the polymer membrane and also holds the membrane's dimensional stability, which are the significant benefits of using sulfonated inorganic additives. The membrane contains higher dimensional stability with hydrophilic nature, and an acid functional group can effectively transfer the protons from the anode to the cathode via the vehicular (diffusion) mechanism and Grotthuss (hopping) mechanism. This phenomenon generates more ionic channels and carriers for efficient proton transport. Thus, the overall performance of MFC-containing hybrid (organic polymers and inorganic-sulfonated additives) composite membranes has been higher than that of commercial membranes and corresponding pure polymer membranes. To further improve the overall performance of membrane for MFC applications, numerous efforts can be made by developing the inorganic additives with various concepts: (i) dimensional modifications (e.g., developing 2D-structured inorganic additives containing proton exchange site will be more effective in controlling the crossover of oxygen without affecting the proton transport behavior); (ii) functionalization of different properties of inorganic additives (Very limited inorganic additives have been studied as a nanofiller for MFC membranes. Therefore, excellent inorganic additives can be identified using various options with different functionalization.); and (iii) combinations with different kinds of organometallics and inorganic polymers.

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