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Polymeric nanocomposites for innovative functional enhancement of electrodes and proton exchange membrane in microbial fuel cell

ABDUL AZEEZ OLAYIWOLA SIRAJUDEEN and M. SUFFIAN M. ANNUAR*

*Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603,
Kuala Lumpur, Malaysia*

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Abstract: Practical application of microbial fuel cell (MFC), a sustainable energy device, is hampered by low power output. Its principal components *i.e.*, anode, cathode and proton exchange membrane (PEM) are the focus of enhancement and modification in terms of their functional design and material. The anode surface conduciveness as electron sink is crucial to the power output magnitude, while the cathode electrode should be reactive for efficient oxygen reduction at tri-phase junction. PEM is solely responsible for unidirectional proton flow concomitantly completing the electrical circuit. Polymeric nanocomposites as electrode modifier improved significantly anode/cathode/PEM functions thus overall MFC performance. The review highlights the progress made in polymer-based modifications to anode, cathode and PEM material and function between year 2014 to 2019. The effects to biocompatibility, surface area, internal resistance, electrochemical activities, environmental sustainability and overall MFC performance are discussed.

Keywords: anode; cathode; proton exchange membrane; microbial fuel cell; polymeric nanocomposites.

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* Corresponding author. E-mail: suffian_annuar@um.edu.my
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1. INTRODUCTION

The increase in global energy demand due to expanding population and vigorous industrialization has resulted in the search for alternative energy sources that are renewable and ecologically friendly. Energy from fossil fuel are non-renewable, fast depleting and polluting from environmental perspectives. Alternative energy sources, which are green and renewable such as hydrogen fuel,¹ biodiesel,² bioethanol³ and microbial fuel cell (MFC),⁴ are among the focus of intensive research. One of the many possible solutions lies with non-combustion method such as microbial fuel cell. An MFC is a sustainable, promising and nascent energy generation device that combines electricity generation and wastewater treatment through metabolic activities of microorganisms such as *Escherichia coli*, *Geobacter sulfurreducens* and *Shewanella oneidensis*.^{5,6} Its basic design is a two-chambered MFC consists of anode and cathode chambers, and a selective membrane designated as proton exchange membrane (PEM), Fig. 1. Typical anolyte compositions include wastewater, glucose, phosphate buffer, specifically-prepared anolyte containing appropriate amounts of K_2HPO_4 , KH_2PO_4 , $NaCl_2$, $NaHCO_3$, NH_4Cl , $MgSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$ and trace element. Commonly utilized catholyte include phosphate buffer solution, ferricyanide solution, H_2O_2 amongst others. In anode compartment, electrons and hydrogen ions are liberated by the electrogens from biological oxidation of organic matters.⁷ The electrons are transferred to the cathode chamber *via* electrical circuit and the protons pass through PEM for oxygen reduction reaction on the cathode surface, thus completing the redox mechanism.^{7,8} By-products are also produced, *e.g.*, hydrogen peroxide (H_2O_2)⁹ and caustic potash (KOH)^{10,11} at the cathode chamber (Fig. 1).

The two known mechanisms utilized by electrogens for electron transfer to anode surface are direct electron transfer through conductive pili or cytochrome *c* (commonly used by *G. sulfurreducens* and *S. oneidensis*), and mediated electron transfer through secreted redox mediators (commonly used by *E. coli*). Modification of the anode electrode with polymeric nanocomposites has been reported to reduce internal resistance and improve overall MFC performance arising from more efficient extracellular transfer of electrons to the anode surface.¹²⁻¹⁶ A detail review article addressing anode modifications for improved MFC perform-

ance has been presented by Hindatu *et al.*¹² Recent anode modifications with polymeric nanomaterials are discussed herewith.

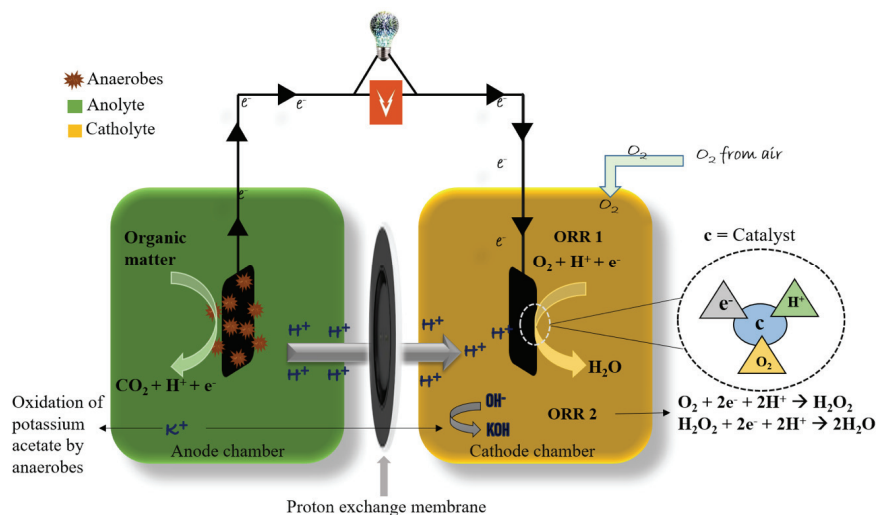


Fig. 1. Schematic overview of a double-chambered MFC.

2. ANODE MODIFICATION WITH POLYMERIC NANOMATERIALS

The anode chamber structure and function are a vital part of MFC set-up. Electrochemically-active bacteria oxidize organic matter liberating electrons and protons in the process. Efficient transfer of electrons to anode surface is crucial to the power output, hence generating overall MFC performance. An efficient anode electrode should support for maximum biofilm colonization and with high affinity as an electron sink. Electrical conductivity, durability and stability, large surface area and porosity amongst others are primary characteristics of a working anode electrode in MFC.^{17–19} Carbon-based nanomaterials have been reported to satisfy these requirements to some extent. However, the hydrophobic nature of these materials strongly hinders maximum bacterial colonization of anode electrode.^{20,21} As such, polymeric nanocomposites of polyesters, conducting polymers and polysaccharides have been studied as anode electrode modifier with some degree of success as discussed in the following sections.

3. NANOCOMPOSITES OF CONDUCTING POLYMERS

3.1. Polypyrrole (PPy)

One widely studied conducting polymer for MFC application is polypyrrole (PPy). Kaur *et al.*²² modified the surface of carbon paper with both pristine and functionalized PPy. The PPy-modified electrode improves the voltage output, the start-up time and stability of maximum voltage generated. Further modification

of PPy with reduced graphene oxide (rGO) nanocomposites (Fig. 2) doubled the power density and recorded a maximum voltage of 400 mV for about 75 h attributed to superior biofilm growth on the modified electrode.²³

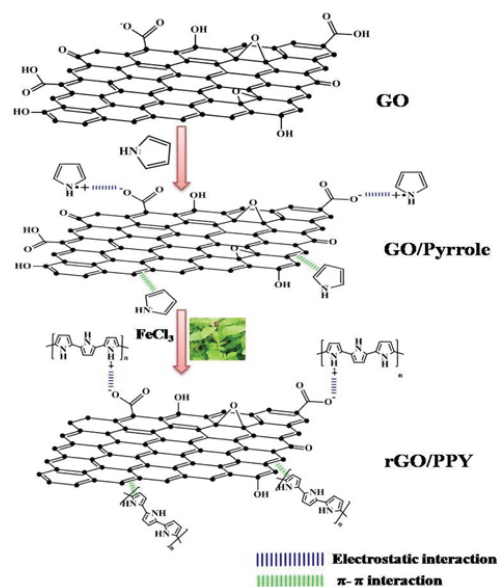


Fig. 2. Proposed mechanism for the preparation of the rGO/PPy composite (reproduced from²³ with permission from American Chemical Society).

One-step electrochemical method is recently employed by Li *et al.*²⁴ to synthesize PPy nanowires and composited it with graphene oxide (GO). The modified anode electrode exhibits functionally superior surface area, improved power density and higher open circuit voltage (OCV). The performance of stainless steel (SS) is significantly enhanced when layered with PPy.²⁵ It results in power density increase of 29-times higher than bare SS anode electrode and a maximum voltage of 547 mV compared to bare SS anode electrode (76 mV).²⁵

3.2. Polyaniline (PANI)

PANI is another conducting polymer widely utilized as anode modifier. Cyclic voltammetry (CV) method has been employed in preparing PANI composited with multi-walled carbon nanotube (MWCNT) through electropolymerization.²⁶ Maximum voltage of almost one volt is recorded with power density of 286 mW/m². Bifunctional catalyst of graphene (G) and TiO₂ with PANI on carbon paper (CP) enhances the performance of MFC.²⁷ The modified electrode shows nearly triple higher power density than plain CP. The internal resistance is reduced by half with the modified electrode set-up. The superior performance is attributed to efficient extracellular electron transfer to anode from favorable colonization of the anode by the bacteria (Fig. 3). Recently, Li *et al.*²⁸ modified

carbon cloth (CC) electrode surface *in situ* using PANI composited with titanium suboxide (TS) and graphene nanoparticles.

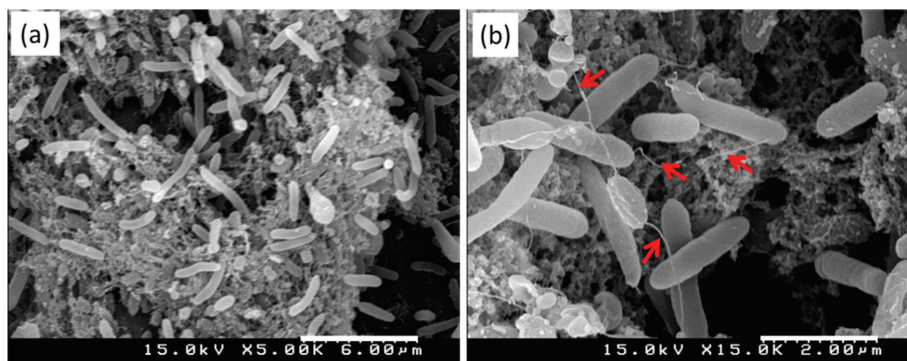


Fig. 3. *Shewanella oneidensis* MR1 morphology enclosed within the matrix of the PANI-TiO₂-GN catalyst at higher and lower magnifications. The red arrows indicate the nanowires of *Shewanella oneidensis* MR1 (reproduced from²⁷ with permission from American Chemical Society).

Longevity in maximum voltage output in modified electrode is evidenced with 13-fold increase in power density compared to bare CC. About 70 % decrease in internal resistance is recorded in PANI-TSG/CC electrode set-up. Similarly, Yellappa *et al.*²⁹ synthesized PANI and PANI/CNT nanoparticles through *in situ* oxidative chemical polymerization, and applied over stainless steel mesh (SSM) surface for wastewater treatment. PANI/CNT-SSM electrode yields 80 % chemical oxygen demand (COD) removal while 65 % is recorded for PANI-SSM and 58 % for bare SSM. Higher OCV is also recorded for polymeric modified electrodes compared to bare SSM. The superiority in PANI/CNT-SSM electrode is attributed to enhanced charge transfer due to incorporation of CNT, which subsequently promotes better conductivity between biocatalyst and anode surface. The studies of Yin *et al.*³⁰ have shown a synergistic effect between TiO₂ nanosheets (TiN) and PANI through electrochemical deposition of PANI onto TiN, at different CV cycles. Maximum power density up to 63.6 % increase is recorded for PANI deposited through 20 CV cycles. Lowest charge transfer resistance is also recorded by the modified electrode with 20 CV cycles.

3.3. Poly(3,4-ethylene dioxythiophene) (PEDOT)

PEDOT is a derivative of polythiophene with superior conductivity compared to PPy and PANI,³¹ also has potential as excellent electrode modifier in MFC. Ma *et al.*³² modified the surface of SS with PEDOT through electrochemical polymerization method. PEDOT/SS electrode recorded six-fold increase in power density compared to bare SS electrode. The current density recorded during MFC operation leveled off at 1150 mA/m² for PEDOT/SS compared to

210 mA/m² for SS electrode (Fig. 4). The efficiency of PEDOT/SS electrode is attributed to dense and conductive film formed on SS plate which not only prevent SS base from biogenic and chemical corrosion, but also improve the electron transport rate to anode.

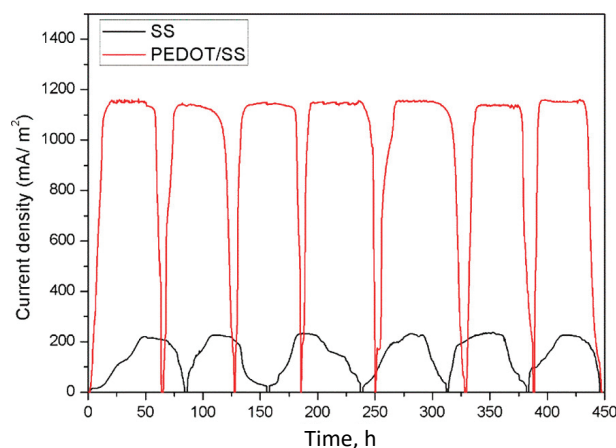


Fig. 4. Power generation in MFCs with an external resistance of 1000 Ω (reproduced from³² with permission from *American Chemical Society*).

Recently, Senthikumar *et al.*³³ modified PEDOT with nickel ferrite nano-rod on biochar as a free-standing electrode. A maximum power density of 1200 mW/m² is recorded, *i.e.*, five times higher than control (ferric oxide on biochar). Further modification of PEDOT polymer matrix with nanoparticles of nickel and rGO (PEDOT/Ni/rGO) results in a power density up to 3200 mW/m² and improve internal resistance and OCV.³⁴ The improved performance of modified electrode is due to homogenous dispersion of the nanoparticles within PEDOT matrix and enhanced biocompatibility between biocatalyst, *i.e.*, *E. coli* and PEDOT/Ni/rGO electrode surface.

3.4. Nanocomposites of polyesters

Polymers with ester functional groups in their main chain are classified as polyesters. Due to their biocompatibility, biodegradability, piezoelectricity, elasticity, durability and resistivity to most chemicals, polyesters have been recently used as anode electrode modifier. Its first utilization in MFC is reported by Luckarift *et al.*³⁵ when 3-polyhydroxybutyrate-*co*-3-hydroxyvalerate (PHBV) is composed with carbon nanofiber by solvent casting method (Fig. 5). Superior biofilm colonization of the modified anode surface results in efficient bioelectrocatalysis, stability and reproducibility in electrolyte with significant power density generation compared to previously reported graphite felt electrode. Hindatu *et al.*⁴ reported the utilization of flexible medium-chain-length polyhydroxyalkanoates

(mcl-PHA) composed of multi-walled carbon nanotube (MWCNT) as CC surface modifier. Maximum power density up to 53 % increase, internal resistance reduction of 31 % and improved maximum voltage of 50 % are recorded for mcl-PHA-MWCNT composite modified electrode compared to pristine CC electrode. Interestingly, further modification of CC surface with amphiphilic mcl-PHA-co-polyethylene glycol methacrylate/MWCNT composite (mcl-PHA-co-PEGMA/MWCNT) further reduce the internal resistance by 97 %, improve the maximum voltage by 75 %, and 74 % enhancement in maximum power density.¹³ It is hypothesized that the superiority in mcl-PHA-co-PEGMA/MWCNT electrode originates from its better biocompatibility and synergistic relationship between the *Escherichia coli* biocatalyst and the modified anode surface. Recently, Sirajudeen *et al.*¹⁶ modified the surface of purified CC with amphiphilic mcl-PHA-co-methyl acrylate composed of functionalized MWCNT as electrode modifier. The modified anode electrode shows improved conductivity, superior redox peak, stable and elevated voltage and enhanced power and current densities, attributed to improved electron transfer rate on modified anode surface.¹⁶ Polycaprolactone (PCL) nano- and micro-fibers have also been composed of gold particles and utilized as anode modifier.³⁶ While high activation loss and high internal resistance are reported, the modified electrode, nonetheless, shows an improved stability of maximum voltage at 600 mV up to 10 days MFC operation. Also, the micro-fiber composite exhibits two-fold increase in power and current densities compared to nano-fiber composite.

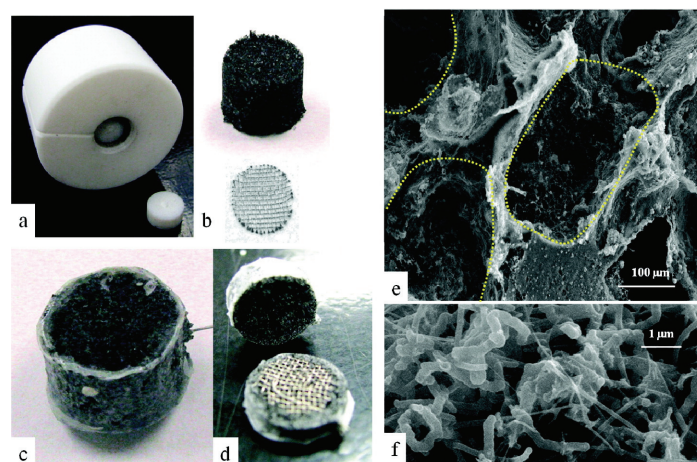


Fig. 5. Visual representation of polymeric nanocomposite fabrication (a). A mold used to: b) pack sucrose/CF around a nickel mesh, c) sucrose/CF scaffold inserted with polymer and d) dissected electrode to reveal the porous scaffold after sucrose removal; e) magnified scaffold with similar size to the original particle indicated by yellow lines; f) scaffold connected with carbon fibers (reproduced from³⁵ with permission from *American Chemical Society*).

3.5. Nanocomposites of polysaccharides

Polysaccharide nanocomposites have been reported as anode modifier. The effects of different nanocomposites *viz.* magnesium and graphite composed alongside chitin particles were investigated.³⁷ Maximum power density of 1872 mW/m² is recorded in magnesium/chitin composite. Chitin supplement is responsible for 121 % increase in magnesium anode, and 164 % increase in graphite anode. The improvement, by chitin-supplemented anode, is attributed to the active growth of bacterial communities on anode surface encouraged by the organic carbon source. A conductive carbon nanotube hydrogel, composed of chitosan, is layered onto carbon paper (CP) surface and applied as anode electrode (Fig. 6).³⁸ A current density peak of 500 mA/m² is recorded for hydrogel modified electrode at a power density of 132 mW/m², compared to raw CP electrode (150 mA/m² of current density). Coulombic efficiency (*CE*) of 32 % is reported for CNT-hydrogel modified electrode while 19 % *CE* for the control. It is suggested that the presence of oxygen-containing functional groups of C=O and C=OH are responsible for high conductivity of the modified electrode. Similarly, Mottet *et al.*³⁹ constructed a conductive composite hydrogel made up of alginate and carbon nanotube. The new electrode shows high compatibility with biocatalyst and better conductivity.

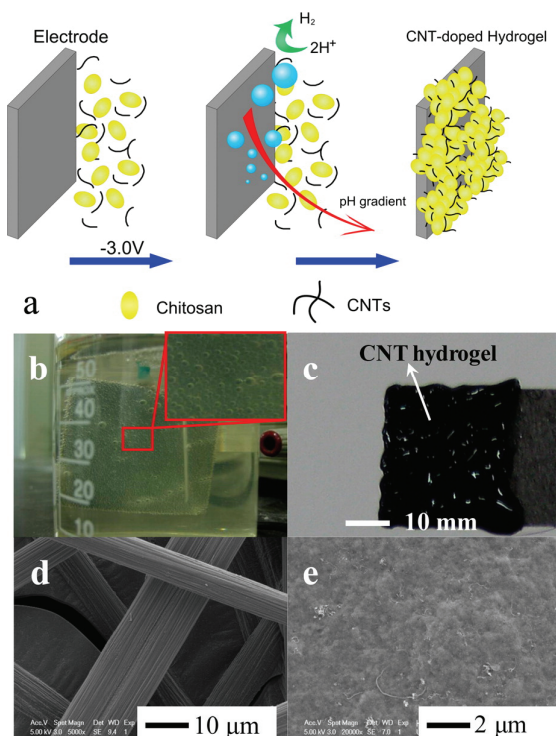


Fig. 6. Visual representations of: a) CNT-hydrogel electrode preparation, b) bubbles generated during the deposition process, c) CNT-hydrogel layered on carbon paper, d) SEM images of carbon paper and e) CNT-hydrogel/carbon paper composite (reproduced from³⁸ with permission from *American Chemical Society*).

3.6. Nanocomposites of other polymers

Temperature responsive polymer of poly-*N*-isopropylacrylamide (PNIPAM) has been investigated as anode modifier by Kumar *et al.*⁴⁰ PNIPAM prepared with CNT and GO nanoparticles is subsequently structured into hydrogel (Table I). Pristine PNIPAM electrode records a power density peak of 43 mW/m² at a current density of 453 mA/m². The incorporation of CNT into PNIPAM matrix results in six-fold increase of power density, *i.e.*, 264 mW/m² at a current density of 2502 mA/m². Further modification with GO nanoparticles results in significant increase in both power and current densities at 434 mW/m² and 3603 mA/m², respectively. The decrease in charge transfer resistance of PNIPAM is attributed to synergistic interaction between two highly conductive nanoparticles, *viz.* CNT and GO that concomitantly improve the MFC performance with a longevity of more than 300 h. Recently, Chen *et al.*⁴¹ reported hydrogel formation of polyacrylamide (PAM) with rGO and graphite brush (GB) as current collector through *in situ* polymerization method, followed by reduction with ascorbic acid. The PAM/rGO/GB electrode records 34.8 % increase in maximum power density compared to GB anode. Superiority in CE is observed for PAM/rGO/GB electrode at 35.6 % compared to GB electrode (21.1 %). Close proximity of the biofilm to anode surface as well as large surface area afforded by modified electrode are suggested to be responsible for the enhanced MFC performance. Polymeric derived ceramics (PDC) route has been employed in making a highly conductive hydrophilic polymeric nanocomposite of polymethylsilsesquioxane and poly(methyl-phenylsilsesquioxane) composed of graphite and carbon black.⁴² The

TABLE I. Typical anode materials, polymer and carbon loadings for anode modification

Anode material	Type of polymer loading	Type of C/metal loading	Reference
rGO	PPy	Graphite powder	Kumar <i>et al.</i> ²³
Nickel plate	PPy nanowires	GO	Li <i>et al.</i> ²⁴
CC	PANI	MWCNT	Wang <i>et al.</i> ²⁶
CP	PANI	Graphene/TiO ₂	Han <i>et al.</i> ²⁷
CC	PANI	Graphene/Ti ₄ O ₇	Li <i>et al.</i> ²⁸
SSM	PANI	CNT	Yellappa <i>et al.</i> ²⁹
CP	PANI	TiO ₂ nanosheet	Yin <i>et al.</i> ³⁰
Biochar	PEDOT	Nickel ferrite nanorod	Senthilkumar <i>et al.</i> ³³
SS	PEDOT	Graphene/Nickel	Hernandez <i>et al.</i> ³⁴
CC	mcl-PHA	MWCNT	Hindatu <i>et al.</i> ⁴
CC	mcl-PHA/PEGMA	MWCNT	Yusuf <i>et al.</i> ¹³
CP	PCL	CNT/CNF/Gold	Fraivan <i>et al.</i> ³⁶
CC	mcl-PHA/Methyl acrylate	MWCNT	Sirajudeen <i>et al.</i> ¹⁶
CC	Chitin	Graphite/Magnesium	Jung <i>et al.</i> ³⁷
CP	Chitosan	CNT	Liu <i>et al.</i> ³⁸
CC	PNIPAM	Graphene/CNT	Kumar <i>et al.</i> ⁴⁰
Graphite brush	Polyacrylamide	rGO	Chen <i>et al.</i> ⁴¹

novel anode material records two-fold increase in power density (211 mW/m^2) compared to carbon felt anode (111 mW/m^2). When the MFC system is applied for wastewater treatment, similar COD removal rate and CE are recorded for modified and pristine anode electrodes. The high specific surface area of the modified anode as well as its porous structure results in superior biocompatibility as evidenced by extensive biofilm growth on the electrode surface, and consequently improve electron transfer process.⁴²

4. CATHODE MODIFICATION

Although MFC is a clean, sustainable, renewable and earth-friendly electricity generating device, low power output generated by the technology hampers its widespread practical applications.¹² To tackle this issue, the cathode electrode that determines catalytic activities of terminal electron acceptors, is a rational target to be modified accordingly. The primary challenge in fabricating an effective cathode electrode is keeping its surface highly conductive and catalytically-active for a prolonged period of MFC operation.⁴³ A practical cathode electrode should also be inexpensive and readily available,⁴⁴ easy to fabricate,^{45,46} electrocatalytically efficient⁴⁷ and stable in catholyte.⁴⁸ Factors such as concentration of protons,^{48–50} electrode spacing,⁵¹ and electrode surface area⁵² are known to affect electrocatalytic activities of the cathode electrode. Some commonly utilized materials and their respective loadings when applied as a component to improve electrocatalytic function of a cathode are carbon nanotube (5 mg/cm^2),⁴ KMnO_4 (2 mg/cm^2), platinum (0.048 mg/cm^2)²⁰ amongst others. An extensive review on carbon-based polymer nanocomposites as cathode electrode material for MFC is provided by Jafary *et al.*²⁰ Significant improvements are evidenced in polymer-based modification of cathode electrodes compared to bare electrode materials. The development of a stable, efficient, polymer-based (modified) cathode electrode that enhances interfacial electrochemical reaction will significantly increase the power output of MFC, and a step closer towards its adoption in various applications.

4.1. Cathode modification with polymeric nanomaterials

Ahmad *et al.*⁵³ constructed MFC setup with PANI nanofibers prepared with carbon black. Higher electrochemical activities, with power density improvement up to 2.7-fold increase, is obtained with the composite cathode compared to pristine PANI (control). Although the power density is still lower than Pt-based electrode, the environmental-friendly polymeric composite is economically feasible when considering large-scale applications. Sulfonated PANI (SPANI), composed of highly efficient bimetallic nanocomposites of 1:1 nickel (Ni) and cobalt (Co), is investigated by Papiya *et al.*⁵⁴ for cathode electrode modifier. Spectroscopic analyses indicate the nanocomposites to be well distributed on the supporting matrix. When compared with the controls, the highest catalytic activity is obs-

erved in SPANI/Ni-Co electrode with a maximum power density at 659 mW/m^2 relative to Pt-based electrode at 483 mW/m^2 . Incorporation of highly functional nanoparticles of graphene and TiO_2 into PANI matrix to enhance the reduction of oxygen at cathode has also been reported.²⁷ The ternary nanocomposite exhibited superior rate of oxygen reduction activity compared to controls (pristine PANI and PANI/ TiO_2 electrodes).

Polypyrrole (PPy) is another conducting polymer that has been utilized as cathode modifier. A solvothermal method is employed to synthesize a novel composite of manganese, PPy and carbon nanotube.⁵⁵ The composite demonstrated efficiency and stability as cathode catalyst for oxygen reduction reaction. A power density peak of 213 mW/m^2 at a material loading rate of 2 mg/cm^2 is recorded, comparable to platinum/carbon black composite electrode. Further modification of PPy polymer matrix with MnO_2/CNT composite using cost-effective hydrothermal method results in an improved maximum power density of 721 mW/m^2 .⁵⁶ Improved long-term stability of the composite electrode compared to Pt/C electrode is also reported, making the electrode an alternative to Pt/C electrode for sustainable energy generation.

A single-chambered MFC has been developed by coating the air-facing side with poly(dimethylsiloxane) prepared with nitrogen-doped nickel nanoparticles and carbon nanofibers. The polymer-metal-carbon nanocomposite shows high efficiency in oxygen reduction reaction in MFC, serving as an ideal alternative to potentially harmful Pt-based and Nafion electrode.⁵⁷ Ong *et al.*⁵⁸ recently have synthesized a polymeric cathode composed of polyvinylpyrrolidone/carbon nanotube/manganese oxide (P/ MnO_2/CNT) for air cathode MFC. Electrochemical analyses reveal higher oxygen reduction reaction activities with low charge transfer resistance compared to control electrodes of MnO_2 and MnO_2/CNT . When utilized in MFC, a maximum power density of 91 mW/m^2 is recorded, which is significantly higher than MnO_2/CNT catalyst (72 mW/m^2), MnO_2 catalyst (36 mW/m^2) and CNT catalyst (29 mW/m^2). Also, relatively high COD removal percentage of 74 % is recorded for the P/ MnO_2/CNT electrode.

One of the most recent modifications involving polymeric cathode nanocomposite utilizes polysaccharide-carbon composite. A bacterial cellulose doped with particles of phosphorus and copper is used as cathode catalyst in MFC⁵⁹ (Fig. 7). A three-dimensional structure with extensive large surface area is fabricated. Improvement in the catalytic activity of the polymeric nanocomposite is attributed to the increase in active sites from Cu and P doping.

A maximum power density of 1177 mW/m^2 at a current density of 6730 mA/m^2 is recorded, significantly higher than Pt-based electrode (1044 mW/m^2 at a current density of 6020 mA/m^2). A five-fold increase in power density is observed when a cathode electrode is modified with a dual-doped carbon derived from chitosan.⁶⁰ Improved internal resistance, high open circuit voltage as well

as large surface area of about $982 \text{ m}^2/\text{g}$, resulting in better oxygen mass transfer are attributed to better performance in the nitrogen- and phosphorus-doped electrodes.

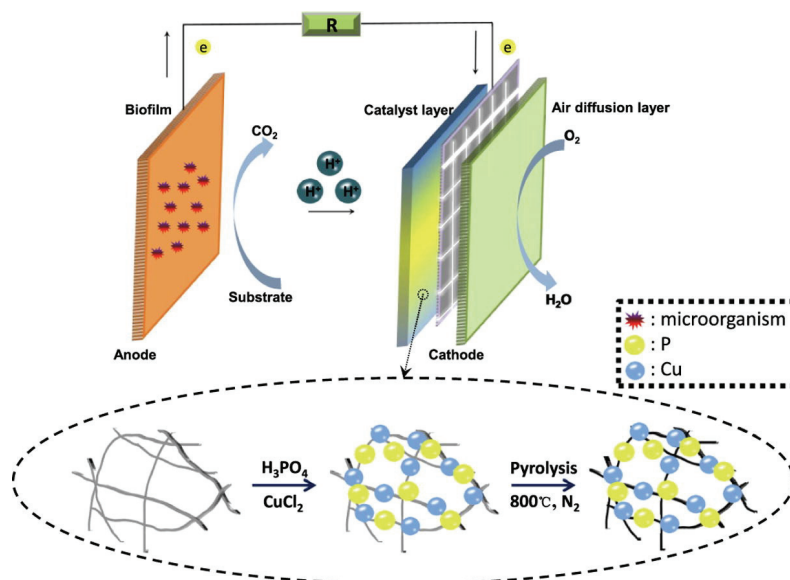


Fig. 7. Schematic diagram of bacterial cellulose doped with phosphorus and copper via freeze-drying and high-temperature pyrolysis (reproduced from⁵⁹ with permission from *Elsevier*).

5. PROTON EXCHANGE MEMBRANE (PEM)

The primary function of PEM in MFC is to separate the anode and cathode electrolytes, and simultaneously allow for maximum proton (H^+) passage from anode to cathode chamber. However, high cost and environmentally detrimental nature of some widely utilized PEM warrant for the development of alternative, efficient, readily available, economical, and environmental friendly PEMs. The recent advancements in PEM fabrication for MFC application are discussed in the following sections.

5.1. Polyether ether ketone (PEEK) nanocomposites as PEM

Quaternized PEEK (QPEEK) and sulfonated PEEK (SPEEK) are fabricated and utilized as anion and cation exchange membranes, respectively.⁶¹ Superiority of QPEEK as exchange membrane is observed with maximum power density of $603 \text{ mW}/\text{m}^2$ and CE of 76 % compared to SPEEK ($458 \text{ mW}/\text{m}^2$ and 61 %). SPEEK allows for more cation transport instead of protons, and exhibits high pH gradient. It results in the formation of chemical precipitate on cathode surface and subsequently, high internal resistance and MFC deterioration. SPEEK mem-

branes are fabricated with different degrees of sulfonation (DS) (20.8, 41, 63.6 and 76 %) for MFC application.⁶² SPEEK with 63.3 % DS exhibits the highest power density (68.64 mW/m²), COD removal (91 %) and CE (26 %). Although power density generation is still lower than Nafion membrane (74.8 mW/m²), cost estimation suggests that the utilization of SPEEK with 63 % DS is a feasible alternative due to high power generation per cost. Further modification of the SPEEK membrane with hybridization of polysulfone (PS) at lower and higher DS for desalination and power generation has also been investigated.⁶³ The degree of porosity of the modified membrane is in direct proportion to DS as shown in Fig. 8. The amphiphilic hybrid membrane with 29 % DS exhibits the highest power density and significantly high NaCl (62 %) and MgSO₄ (68 %) rejection rate notwithstanding lower than PS/SPEEK (76 %) for NaCl (67 %) and MgSO₄ (81 %) rejection rate. Particles of silicotungstic acid are entrapped into the matrix of SPEEK through phase inversion method.⁶⁴ The hybrid composite membrane shows reduced oxygen gas crossover, which results in four-fold increase in the generation of maximum power density compared to Nafion membrane.

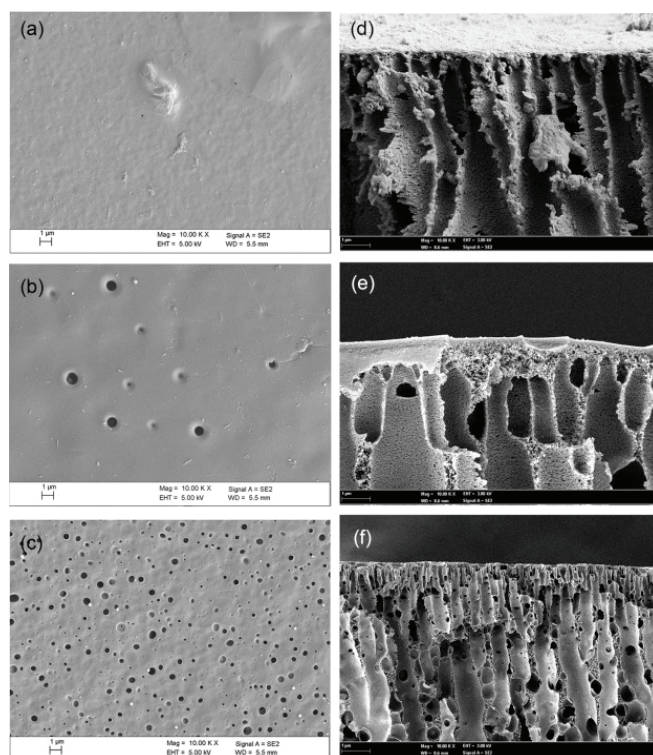


Fig. 8. SEM images of: a) surface of PS, b) surface of PS/SPEEK (29 %), c) surface of PS/SPEEK (76 %), d) cross section of PS, e) cross section of PS/SPEEK (29 %) and f) cross section of PS/SPEEK (76 %) (reproduced from⁶³ with permission from *Elsevier*).

5.2. Nafion nanocomposites as PEM

While neat Nafion is the most utilized PEM in MFC, enhancement of its performance through composites of nanoparticles has also been investigated. Angi-*oni et al.*⁶⁵ modified Nafion membrane with functionalized SB-15 silica. Functionalization is done with SO₃H group and applied as PEM in an extended MFC operation. Nafion-based SB-15 composite of 15 mass % is found to exhibit maximum power density, three times higher than neat Nafion after three months of MFC operation. The same membrane offers high resistivity to biofouling, high COD removal of 95 % after 14 days and also improve *CE* recovery of 34 %. The efficiency of the modified PEM is attributed to the presence of the silica-based SO₃H functionalized filler. Bajestani *et al.*⁶⁶ investigated the effects of different solvents in a process where Nafion is composited with TiO₂ through solvent casting method. Nafion composite with dimethylformamide (DMF) solvent yields the highest OCV, proton conductivity and the highest membrane porosity. Alumina nanoparticles (Al₂O₃) ranging 5–20 mass % are incorporated within the matrix of sulfonated poly-(vinylidene fluoride-hexafluoropropylene) (PVDF-*co*-HFP) blended with Nafion at different molar ratios.⁶⁷ Increase in water uptake is observed with increased incorporation of Al₂O₃ nanoparticles. Membrane with 5 mass % nano Al₂O₃ shows superior proton conductivity and improved maximum power and current densities of 48 and 11 %, respectively. Hernandez *et al.*⁶⁸ developed membranes of agar prepared with Nafion liquid and tested them against Nafion 117 membrane. Reduced internal resistance is observed in all modified membranes from incorporation of agar. Although the power densities are lower than the control, *i.e.*, Nafion 117 membrane, higher power/cost ratio is deemed to be an advantage in agar composite membranes than Nafion membrane.

5.3. Chitosan and polyester nanocomposites as PEM

A low-cost polyester cloth (PC) with varying layers are utilized as PEM in MFC and compared with Nafion membrane.⁶⁹ Higher mass transfer and reduced diffusion coefficient of oxygen are observed in PC membranes compared to Nafion. A comparable internal resistance, power and current densities are observed in PC membranes and Nafion membrane, indicating a possible alternative to health hazard Nafion. In another PEM investigation, Yusuf *et al.*⁷⁰ demonstrated for the first time the application of biodegradable microbial polyester, *i.e.*, medium-chain-length polyhydroxyalkanoates prepared with functionalized multi-walled carbon nanotubes (mcl-PHA/MWCNT) at varying amount (5–20 mass %), obtained through ultrasound dispersion blending method. Comparable power density to Nafion membrane is recorded. However, membrane with 10 % MWCNT is superior in COD removal percentage, *CE*, conductivity and reduced internal resistance over Nafion membrane. Recently, Sirajudeen *et al.*⁷¹ incorporated different amount of polyhydroxybutyrate (PHB) crystal (5–15 mass %) into

mcl-PHA matrix through solvent blending method. The composite biopolymer was investigated as an alternative PEM to Nafion in a double-chambered MFC with real wastewater as substrate. Composite with 10 and 15 % PHB show superior maximum voltage at 988 and 1001 mV, respectively, compared to Nafion (594 mV). Better power density is also recorded for PHB15% (601 mW/m²) compared to Nafion (520 mW/m²). Superiority in overall MFC performance of composite membrane is attributed to better water uptake and wettability, as well as higher resistivity of the novel membrane to gas flux from cathode to anode compartment. Harewood *et al.*⁷² investigated thermal condensation of malic and citric acid in 3:1 ratio and its blend with chitosan. The copolymer is utilized as PEM in MFC. The maximum power and current densities generated are comparable to Nafion 117 membrane. The copolymer is biodegradable, thus making it another environmental friendly alternative to Nafion membrane. Furthermore, the effects of applying different cross-linkers are investigated by Holder *et al.*⁷³ Graphene oxide nanoparticles are incorporated into the matrix of chitosan and cross-linked with either phosphoric- or sulfuric acid. Phosphoric acid cross-linked PEM shows 135 % increase in power density compared to sulfuric acid cross-linked PEM.

5.4. Ceramics and polyethersulfone (PES) nanocomposites

Polyethersulfone (PES) is sulfonated with chlorosulfonic acid (SPES) and finally blended with pristine PES (PES/SPES).⁷⁴ The PES/SPES as exchange membrane shows superiority in COD removal percentage, CE, oxygen permeability, biofouling and power generation compared to Nafion membrane. Di Palma *et al.*⁷⁵ recently developed a type of membrane where PES is prepared with different concentrations of Fe₃O₄ nanoparticles using melt-blend method. PES with 20 % Fe₃O₄ nanoparticles generated maximum power density of 9.59 mW/m² and current density of 38 mA/m². Incorporation of the nanoparticles of more than 20 mass % leads to fissuring of the membrane. Similar observation has also been reported by Yusuf *et al.*⁷⁰ In another study, ceramic membranes with different pore sizes (0.14 μm, 150 and 5 kDa) are investigated as PEM in MFC and compared with cation exchange membranes and Nafion membrane.⁷⁶ Ceramic membrane with the largest pore size, *i.e.*, 5 kDa shows improved power density, better CE and reduced internal resistance compared to other membranes. When the surface wall of ceramic is layered with films of chitosan and montmorillonite minerals,⁷⁷ membranes with six layers and above record a decrease of six-fold in the oxygen gas crossover, resulting in two-fold maximum power density in membrane with seven bi-layers compared to pristine ceramic membrane.

5.5. Nanocomposites of other materials as PEM

Hernandez *et al.*⁷⁸ developed a polymer inclusion membrane based on different weight percentage of ionic liquid as PEM in MFC application. Ionic liquid of 1-octyl-3-methylimidazolium hexafluorophosphate and methyl trioctyl ammonium chloride are utilized. Maximum power density of up to 30 mW/m² and COD removal efficiency of 80 % are recorded for membrane inclusion of 70 mass % ionic liquid supported with ammonium. The increase in ionic liquid concentration is followed by power density increase. In another study, synthetic fiber of polybenzimidazole (PBI) is fabricated with different amounts of polyvinylpyrrolidone (PVP) and utilized as PEM in MFC.⁷⁹ About 81 % increase in power output and superior COD removal percentage are observed in composite membrane with 70:30 PVP:PBI over pure PBI membrane, indicating the utility of PVP as composite membrane in MFC. Similarly, PBI has been fabricated with mesostructure of SB-15 silica as PEM in a long-term MFC operation for wastewater treatment.⁸⁰ The cost-efficient composite membrane shows an order of magnitude increase in maximum power density compared to Nafion, and about 31 % CE and 90 % COD removal are observed (Table II).

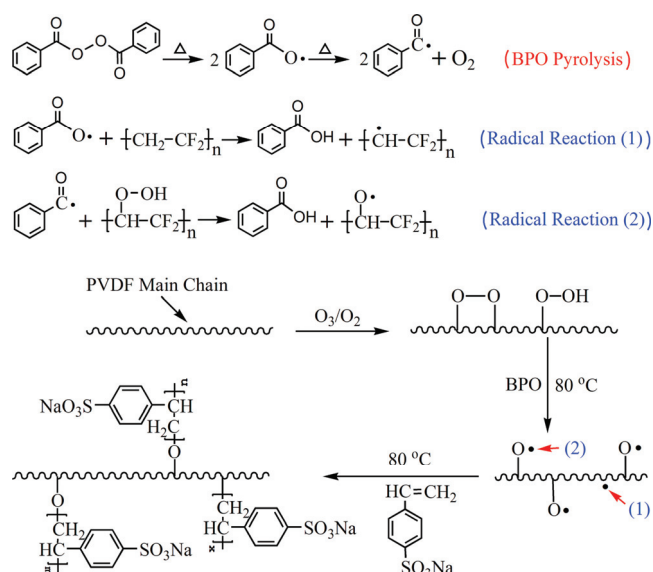
Blending of sulfonated SiO₂ (S-SiO₂) with sulfonated polystyrene ethylene butylene polystyrene (SSEBS) is investigated as yet another alternative to Nafion membrane. Various percentages of S-SiO₂ ranging 2.5–10 mass % are studied.⁸¹ The modified membranes show superior power density over Nafion, with 7.5 % S-SiO₂ membrane exhibiting four-fold increase in power density (1209 mW/m²) over Nafion (290 mW/m²). S-SiO₂ incorporation is suggested to be responsible for enhanced proton conductivity. In a separate study, Li *et al.*⁸² thermally grafted an ozone-pretreated poly(vinylidene fluoride) (PVDF) with sodium styrene sulfonate (SSS) as shown in Fig. 9. Better COD removal percentage (85 %) is observed using the cost-efficient copolymer compared to Nafion membrane (74 %). Although, higher power density is recorded for Nafion membrane (132.0 mW/m²) compared to the modified membrane (106.7 mW/m²), cost/power ratio of the modified membrane makes it an efficient alternative to Nafion.

TABLE II. Comparison of reported membranes in terms of thickness, water uptake, COD, CE, and power density

Membrane	Thickness mm	Water uptake, %	COD %	CE %	Power density mW m ⁻²	Reference
SPEEK	0.03	15	–	61	458	Elangovan &
QPEEK	0.03	23	–	76	603	Dharmalingam ⁶¹
SPEEK + PS	–	22	86	22.4	97.47	Ghasemi <i>et al.</i> ⁶³
STA+ SPEEK	0.19	22	–	–	207	Venkatesan & Dharmalingam ⁶⁴
Mesoporous silica + Nafion 117	0.06	–	95	34	25.86	Angioni <i>et al.</i> ⁶⁵

TABLE II. Continued

Membrane	Thickness mm	Water uptake, %	COD %	CE %	Power density mW m ⁻²	Reference
Nano Al ₂ O ₃ + PVDF-co-HFP + Nafion	0.02 – 0.021	24	86.62	3.3	541	Kumar <i>et al.</i> ⁶⁷
mcl-PHA + MWCNT	0.176	33	91	26	361	Yusuf <i>et al.</i> ⁷⁰
mcl-PHA + PHB	0.149	22	72.7	65.7	601	Sirajudeen <i>et al.</i> ⁷¹
Chitosan + GO	–	60	89.52	–	1.11	Holder <i>et al.</i> ⁷³
PES + SPES	0.25	68.6	82	22	58.7	Zinadini <i>et al.</i> ⁷⁴
PES + Fe ₃ O ₄	0.2 – 0.35	1.59	75	11.36	9.57	Di Palma <i>et al.</i> ⁷⁵
Ceramic membrane	24	–	89	41	1790	Daud <i>et al.</i> ⁷⁶
Polymer inclusion + Ionic liquid	0.25	–	80	12	30.6	Hernandez-Fernandez <i>et al.</i> ⁷⁸
PBI + PVP	–	35.4	84.36	–	231.38	Kumar <i>et al.</i> ⁷⁹
PBI + SBA-15	0.04	–	73	14	103.5	Angioni <i>et al.</i> ⁸⁰
SSEBS + SiO ₂	0.18	210	–	85	1209	Sivasankaran <i>et al.</i> ⁸¹
PVDF-g-SSS	0.1	25	85	5.96	106.7	Li <i>et al.</i> ⁸²

Fig. 9. Schematic representation of ozone pretreatment of PVDF and graft copolymerization of SSS (reproduced from⁸² with permission from Elsevier).

6. CONCLUSION

Innovative technologies, such as microbial fuel cell (MFC), offer the conversion of chemical energy from waste into renewable energy. While the electrochemistry of the device is well-established, the next level progress towards its practical applications rests wholly within the material science aspect of the tech-

nology. In the current narrative of sustainable and zero detriment towards the environment, and with ever increasing demand and pressure to shift towards materials that fit such bill, biodegradable polymeric nano-composition approach is the most feasible and practical. It offers functional compatibilities with vast majority of electro-conductive nanomaterials, and the subsequent seamless integration of the composites as apparatus in the MFC device is extremely useful. Furthermore, natural bio-compatibility of the biopolymeric nanocomposites with electrogens when applied as anode surface modifier will significantly improve the electron transfer efficiency. Intensive research efforts to extensively explore novel formulation of bio-degradable polymeric nano-composition and its innovative integration as functional and structural components in the MFC device will be instrumental in advancing the technology to practical and sustainable wide applications.

ABBREVIATIONS

MFC	- Microbial fuel cell
PEM	- Proton exchange membrane
mcl-PHA	-Medium-chain-length polyhydroxyalkanoates
PEGMA	- Poly(ethylene glycol) methyl acrylate
MA	- Methyl acrylate
CV	- Cyclic voltammetry
CNT	- Carbon nanotube
MWCNT	- Multi-walled carbon nanotube
CNF	- Carbon nanofiber
CC	- Carbon cloth
CP	- Carbon paper
SS	- Stainless steel
SSM	- Stainless steel mesh
COD	- Chemical oxygen demand
CE	- Coulombic efficiency
PPy	- Polypyrrole
PANI	- Polyaniline
PEEK	- Polyether ether ketone
PEDOT	- Poly(3,4-ethylene dioxythiophene)
G	- Graphene
GO	- Graphene oxide
rGO	- Reduced graphene oxide
OCV	- Open circuit voltage
SPEEK	- Sulfonated polyether ether ketone
QPEEK	- Quaternized polyether ether ketone
PS	- Polysulfone
PVDF	- Poly(vinylidene fluoride)
PVDF-co-HFP	- Poly-(vinylidene fluoride-hexafluoropropylene)
PES	- Polyethersulfone
SPES	- Sulfonated polyethersulfone

PBI	- Polybenzimidazole
PVP	- Polyvinylpyrrolidone
SSEBS	- Sulfonated polystyrene ethylene butylene polystyrene
SSS	- Sodium styrene sulfonate

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ИЗВОД

ПОЛИМЕРНИ НАНОКОМПОЗИТИ ЗА ИНОВАТИВНО ФУНКЦИОНАЛНО
ПОБОЉШАЊЕ ЕЛЕКТРОДА И МЕМБРАНЕ ЗА РАЗМЕНУ ПРОТОНА У МИКРОБНОЈ
ГОРИВНОЈ ЂЕЛИЈИ

ABDUL AZEEZ OLAYIWOLA SIRAJUDEEN и M. SUFFIAN M. ANNUAR

Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia

Практичну примена микробних горивних ћелија (MFC), одрживог енергетског уређаја, ограничава мала излазна снага. Његове главне компоненте, тј. анода, катода и протонска мембрана за измену (PEM) представљају основни фокус унапређења и модификација у смислу њиховог функционалног дизајна и материјала. Површинска проводљивост аноде као понор електрона пресудна је за величину излазне снаге, док би катодна електрода требало да буде реактивна за ефикасну редукцију кисеоника на трифазном спајању. PEM је једини одговоран за једносмерни ток протона који истовремено прави струјно коло. Полимерни наноконтрополимери као модификатор електрода значајно су побољшали функције аноде/катоде/PEM, чиме су остварили укупне перформансе MFC. Овај прегледни рад наглашава напредак у модификацијама аноде, катоде и PEM материјала полимерима од 2014. до 2019. године. Дискутује се о ефектима на биокомпатибилност, површину, унутрашњу отпорност, електрохемијску активност, одрживост и свеукупне перформансе MFC.

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REFERENCES

1. X. Jie, S. Gonzalez-Cortes, T. Xiao, J. Wang, B. Yao, D. R. Slocombe, P. P. Edwards, *Angew. Chem. Int. Ed. Engl.* **56** (2017) 10170 (<https://doi.org/10.1002/anie.201703489>)
2. S. Kanimozhi, K. Perinbam, in *Proceedings of the 3rd ISESCO International Workshop and Conference on Nanotechnology 2012 (IWCN2012)*, *J. Phys: Conf. Ser.* (2012), Selangor, Malaysia, IOP Publishing LTD, Selangor, 2013, p. 431
3. A. Parmar, N. K. Singh, A. Pandey, E. Gnansounou, D. Madamwar, *Bioresour. Technol.* **102** (2011) 10163 (<https://doi.org/10.1016/j.biortech.2011.08.030>)
4. Y. Hindatu, M. Annuar, R. Subramaniam, A. Gumel, *Bioproc. Biosys. Eng.* **40** (2017) 919 (<https://doi.org/10.1007/s00449-017-1756-4>)
5. A. Almatouq, A. O. Babatunde, *Appl. Energy* **230** (2018) 122 (<https://doi.org/10.1016/j.apenergy.2018.08.108>)
6. F. Yu, C. Wang, J. Ma, *Materials* **9** (2016) 807 (<https://doi.org/10.3390/ma9100807>)
7. B. E. Logan, *Nat. Rev. Microbiol.* **7** (2009) 375 (<https://doi.org/10.1038/nrmicro2113>)
8. L. Xiao, Z. He, *Graphene-Based Energy Devices* **13** (2015) 355 (<https://doi.org/10.1002/9783527690312.ch13>)
9. L. Fu, S. J. You, F. L. Yang, M. M. Gao, X. H. Fang, G. Q. Zhang, *J. Chem. Technol. Biot.* **85** (2010) 715 (<https://doi.org/10.1002/jctb.2367>)
10. I. Gajda, J. Greenman, C. Melhuish, C. Santoro, I. Ieropoulos, *Bioresour. Technol.* **215** (2016) 285 (<https://doi.org/10.1016/j.biortech.2016.04.004>)

11. I. Gajda, J. Greenman, C. Melhuish, C. Santoro, B. Li, P. Cristiani I. Ieropoulos, *Water Res.* **86** (2015) 108 (<https://doi.org/10.1016/j.watres.2015.08.014>)
12. Y. Hindatu, M. Annuar, A. Gumel, *Renew. Sustain. Energy Rev.* **73** (2017) 236 (<https://doi.org/10.1016/j.rser.2017.01.138>)
13. H. Yusuf, M. S. M. Annuar, R. Subramaniam, A. M. Gumel, *Chem. Eng. Technol.* **42** (2018) 566 (<https://doi.org/10.1002/ceat.201800023>)
14. H. F. Cui, L. Du, P. B. Guo, B. Zhu, J. H. Luong, *J. Power Sources* **283** (2015) 46 (<https://doi.org/10.1016/j.jpowsour.2015.02.088>)
15. Y. L. Kang, S. Ibrahim, S. Pichiah, *Bioresour. Technol.* **189** (2015) 364 (<https://doi.org/10.1016/j.biortech.2015.04.044>)
16. A. A. O. Sirajudeen, M. S. M. Annuar, R. Subramaniam, *Biotechnol. Appl. Biochem.* **00** (2020) 1 (<https://doi.org/10.1002/bab.1928>)
17. A. Baudler, I. Schmidt, M. Langner, A. Greiner, U. Schröder, *Energy Environ. Sci.* **8** (2015) 2048 (<https://doi.org/10.1039/c5ee00866b>)
18. T. Huggins, H. Wang, J. Kearns, P. Jenkins, Z. J. Ren, *Bioresour. Technol.* **157** (2014) 114 (<https://doi.org/10.1016/j.biortech.2014.01.058>)
19. S. H. Lee, J. Y. Ban, C. H. Oh, H. K. Park, S. Choi, *Sci. Rep.* **6** (2016) 28588 (<https://doi.org/10.1038/srep28588>)
20. T. Jafary, M. Ghasemi, J. Alam, S. A. Aljlil, S. Yusup, in *Carbon-based polymer nanocomposites for environmental and energy applications*, A. F. Ismail, P. S. Goh (Eds.), Elsevier, Amsterdam, 2018, pp. 361–390 (<https://doi.org/10.1016/B978-0-12-813574-7.00015-0>)
21. S. Li, C. Cheng, A. Thomas *Adv. Mater.* **29** (2017) 1602547 (<https://doi.org/10.1002/adma.201602547>)
22. A. Kaur, S. Ibrahim, C. J. Pickett, I. S. Michie, R. M. Dinsdale, A. J. Guwy, G. C. Premier, *Sens. Actuators, B* **201** (2014) 266 (<https://doi.org/10.1016/j.snb.2014.04.062>)
23. G. G. Kumar, C. J. Kirubaharan, S. Udhayakumar, K. Ramachandran, C. Karthikeyan, R. Renganathan, K. S. Nahrn, *ACS Sustain. Chem. Eng.* **2** (2014) 2283 (<https://doi.org/10.1021/sc500244f>)
24. X. H. Li, J. S. Qian, X. G. Guo, L. W. Shi, *3 Biotech.* **8** (2018) 375 (<https://doi.org/10.1007/s13205-018-1321-0>)
25. K. B. Pu, Q. Ma, W. F. Cai, Q. Y. Chen, Y. H. Wang, F. J. Li, *Biochem. Eng. J.* **132** (2018) 255 (<https://doi.org/10.1016/j.bej.2018.01.018>)
26. X. Y. Wang, H. B. He, C. C. Zheng, Q. J. Guo, *Particle Sci. Eng.* **347** (2014) 62 (<https://doi.org/10.1039/9781782627432-00062>)
27. T. H. Han, N. Parveen, J. H. Shim, A. T. N. Nguyen, N. Mahato, M. H. Cho, *Ind. Eng. Chem. Res.* **57** (2018) 6705 (<https://doi.org/10.1021/acs.iecr.7b05314>)
28. Z. L. Li, S. K. Yang, Y. N. Song, H. Y. Xu, Z. Z. Wang, W. K. Wang, Y. Q. Zhao, *Int. J. Hydrogen Energy* **44** (2019) 6862 (<https://doi.org/10.1016/j.ijhydene.2018.12.106>)
29. M. Yellappa, J. S. Sravan, O. Sarkar, Y. V. R. Reddy, S. V. Mohan, *Bioresour. Technol.* **284** (2019) 148 (<https://doi.org/10.1016/j.biortech.2019.03.085>)
30. T. Yin, H. Zhang, G. Q. Yang, L. Wang, *Synth. Met.* **252** (2019) 8 (<https://doi.org/10.1016/j.synthmet.2019.03.027>)
31. S. N. J. S. Z. Abidin, M. S. Mamat, S. A. Rasyid, Z. Zainal, Y. Sulaiman, *Electrochim. Acta* **261** (2018) 548 (<https://doi.org/10.1016/j.electacta.2017.12.168>)
32. Q. Ma, K. B. Pu, W. F. Cai, Y. H. Wang, Q. Y. Chen, F. J. Li, *Ind. Eng. Chem. Res.* **57** (2018) 6633 (<https://doi.org/10.1021/acs.iecr.8b00563>)

33. N. Senthilkumar, M. Pannipara, A. G. Al-Sehemi, G. G. Kumar, *New J. Chem.* **43** (2019) 7743 (<https://doi.org/10.1039/C9NJ00638A>)
34. L. A. Hernandez, G. Riveros, D. M. Gonzalez, M. Gacitua, M. A. del Valle, *J. Mater. Sci. Mater. Electron.* **30** (2019) 12001 (<https://doi.org/10.1007/s10854-019-01555-y>)
35. H. R. Luckarift, S. R. Sizemore, K. E. Farrington, J. Roy, C. Lau, P. B. Atanassov, G. R. Johnson, *ACS Appl. Mater. Interfaces* **4** (2012) 2082 (<https://doi.org/10.1021/am300048v>)
36. A. Fraiwan, S. P. Adusumilli, D. Han, A. J. Steckl, D. F. Call, C. R. Westgate, S. Choi, *Fuel Cells* **14** (2014) 801 (<https://doi.org/10.1002/face.201400041>)
37. S. P. Jung, M. H. Yoon, S. M. Lee, S. E. Oh, H. Kang, J. K. Yang, *Int. J. Electrochem. Sci.* **9** (2014) 315
38. X. W. Liu, Y. X. Huang, X. F. Sun, G. P. Sheng, F. Zhao, S. G. Wang, H. Q. Yu, *ACS Appl. Mat. Interf.* **6** (2014) 8158 (<https://doi.org/10.1021/am500624k>)
39. L. Mottet, D. Le Cornec, J. M. Noel, F. Kanoufi, B. Delord, P. Poulin, N. Bremond, *Soft Matter* **14** (2018) 1434 (<https://doi.org/10.1039/C7SM01929G>)
40. G. G. Kumar, S. Hashmi, C. Karthikeyan, A. GhavamiNejad, M. Vatankhah-Varnoos-faderani, F. J. Stadler, *Macromol. Rapid Commun.* **35** (2014) 1861 (<https://doi.org/10.1002/marc.201400332>)
41. J. Y. Chen, P. Xie, Z.P. Zhang, *Chem. Eng. J.* **361** (2019) 615 (<https://doi.org/10.1016/j.cej.2018.12.116>)
42. T. C. D. E. Silva, G. D. Bhowmick, M. M. Ghangrekar, M. Wilhelm, K. Rezwan, *Biochem. Eng. J.* **148** (2019) 29 (<https://doi.org/10.1016/j.bej.2019.04.004>)
43. B. E. Logan, *Microbial fuel cells*, John Wiley & Sons Ltd., New York, 2008, pp. 1–199 (<https://doi.org/10.1002/9780470258590>)
44. V. M. Ortiz-Martinez, M. J. Salar-Garcia, F. J. Hernández-Fernández, A. De los Ríos, *Energy* **93** (2015) 1748 (<https://doi.org/10.1016/j.energy.2015.10.027>)
45. J. R. Kim, G. C. Premier, F. R. Hawkes, R. M. Dinsdale, A. J. Guwy, *J. Power Sources* **187** (2009) 393 (<https://doi.org/10.1016/j.jpowsour.2008.11.020>)
46. H. Liu, B.E. Logan, *Environ. Sci. Technol.* **38** (2004) 4040 (<https://doi.org/10.1021/es0499344>)
47. I. Gajda, J. Greenman, C. Santoro, A. Serov, C. Melhuish, P. Atanassov, I. A. Ieropoulos, *Energy* **144** (2018) 1073 (<https://doi.org/10.1016/j.energy.2017.11.135>)
48. A. Dicks, D.A.J. Rand, *Fuel cell systems explained*, John Wiley & Sons Ltd., New York, 2018, pp. 1–460 (<https://doi.org/10.1002/9781118706992>)
49. P. Mani, T. Keshavarz, T. S. Chandra, G. Kyazze, *Enzyme Microb. Technol.* **96** (2017) 170 (<https://doi.org/10.1016/j.enzmictec.2016.10.012>)
50. F. Zhao, F. Harnisch, U. Schröder, F. Scholz, P. Bogdanoff, I. Herrmann, *Environ. Sci. Technol.* **40** (2006) 5193 (<https://doi.org/10.1021/es060332p>)
51. S. Cheng, H. Liu, B.E. Logan, *Environ. Sci. Technol.* **40** (2006) 2426 (<https://doi.org/10.1021/es051652w>)
52. S. E. Oh, B. E. Logan, *Appl. Microb. Biotechnol.* **70** (2006) 162 (<https://doi.org/10.1007/s00253-005-0066-y>)
53. J. Ahmed, H.J. Kim, S. Kim, *J. Electrochem. Soc.* **159** (2012) B497 (<https://doi.org/10.1149/2.049205jes>)
54. F. Papiya, P. Pattanayak, P. Kumar, V. Kumar, P. P. Kundu, *Electrochim. Acta* **282** (2018) 931 (<https://doi.org/10.1016/j.electacta.2018.07.024>)
55. M. Lu, L. Guo, S. Kharkwal, H. Y. Ng, S. F. Y. Li, *J. Power Sources* **221** (2013) 381 (<https://doi.org/10.1016/j.jpowsour.2012.08.034>)

56. H. Yuan, L. Deng, J. Tang, S. Zhou, Y. Chen, Y. Yuan, *ChemElectroChem* **2** (2015) 1152 (<https://doi.org/10.1002/celec.201500109>)
57. A. Modi, S. Singh, N. Verma, *Int. J. Hydrogen Energy* **42** (2017) 3271 (<https://doi.org/10.1016/j.ijhydene.2016.10.041>)
58. H. R. Ong, C. W. Woon, M. S. Ahmad, A. Yousuf, C. K. Cheng, M. M. R. Khan, *Int. J. Electrochem. Sci.* **13** (2018) 7789 (<https://doi.org/10.20964/2018.08.05>)
59. H. Y. Li, H. Z. Ma, T. Liu, J. Ni, Q. H. Wang, *Bioresour. Technol.* **289** (2019) 121661 (<https://doi.org/10.1016/j.biortech.2019.121661>)
60. B. L. Liang, K. X. Li, Y. Liu, X. W. Kang, *Chem. Eng. J.* **358** (2019) 1002 (<https://doi.org/10.1016/j.ccej.2018.09.217>)
61. M. Elangovan, S. Dharmalingam, *J. Polym. Res.* **23** (2016) 250 (<https://doi.org/10.1007/s10965-016-1136-9>)
62. M. Ghasemi, W. R. W. Daud, J. Alam, Y. Jafari, M. Sedighi, S. A. Aljlil, H. Ilbeygi, *Int. J. Hydrogen Energy* **41** (2016) 4862 (<https://doi.org/10.1016/j.ijhydene.2015.10.029>)
63. M. Ghasemi, W. R. W. Daud, J. Alam, H. Ilbeygi, M. Sedighi, A. F. Ismail, S. A. Aljlil, *Energy* **96** (2016) 303 (<https://doi.org/10.1016/j.energy.2015.12.053>)
64. P. N. Venkatesan, S. Dharmalingam, *Renew. Energy* **102** (2017) 77 (<https://doi.org/10.1016/j.renene.2016.10.027>)
65. S. Angioni, L. Millia, G. Bruni, C. Tealdi, P. Mustarelli, E. Quartarone, *J. Power Sources* **334** (2016) 120 (<https://doi.org/10.1016/j.jpowsour.2016.10.014>)
66. M. B. Bajestani, S.A. Mousavi, *Int. J. Hydrogen Energy* **41** (2016) 476 (<https://doi.org/10.1016/j.ijhydene.2015.11.036>)
67. V. Kumar, P. Kumar, A. Nandy, P. P. Kundu, *RSC Adv.* **6** (2016) 23571 (<https://doi.org/10.1039/C6RA03598A>)
68. G. Hernandez-Flores, H.M. Poggi-Varaldo, O. Solorza-Feria, *Int. J. Hydrogen Energy* **41** (2016) 23354 (<https://doi.org/10.1016/j.ijhydene.2016.08.206>)
69. T. Kim, S. Kang, J. H. Sung, Y. K. Kang, Y. H. Kim, J. K. Jang, *J. Microbiol. Biotechnol.* **26** (2016) 2171 (<https://doi.org/10.4014/jmb.1608.08040>)
70. H. Yusuf, M. S. M. Annuar, S. M. D. Syed Mohamed, R. Subramaniam, *Chem. Eng. Commun.* **206** (2018) 731 (<https://doi.org/10.1080/00986445.2018.1521392>)
71. A. A. O. Sirajudeen, M. S. M. Annuar, K. A. Ishak, Y. Hindatu, R. Subramaniam, *J. Clean Prod.* **278** (2021) 123449 (<https://doi.org/10.1016/j.jclepro.2020.123449>)
72. A. J. T. Harewood, S. R. Popuri, E. I. Cadogan, C. H. Lee, C. C. Wang, *Int. J. Environ. Sci. Technol.* **14** (2017) 1535 (<https://doi.org/10.1007/s13762-017-1258-6>)
73. S. L. Holder, C.H. Lee, S.R. Popuri, *Environ. Sci. Pollut. Res.* **24** (2017) 13782 (<https://doi.org/10.1007/s11356-017-8839-2>)
74. S. Zinadini, A. A. Zinatizadeh, M. Rahimi, V. Vatanpour, Z. Rahimi, *Energy* **125** (2017) 427 (<https://doi.org/10.1016/j.energy.2017.02.146>)
75. L. Di Palma, I. Bavasso, F. Sarasini, J. Tirillo, D. Puglia, F. Dominici, L. Torre, *Eur. Polym. J.* **99** (2018) 222 (<https://doi.org/10.1016/j.eurpolymj.2017.12.037>)
76. S. M. Daud, W. R. W. Daud, B. H. Kim, M. R. Somalu, M. H. Abu Bakar, A. Muchtar, I. S. Chang, *Electrochim. Acta* **259** (2018) 365 (<https://doi.org/10.1016/j.electacta.2017.10.118>)
77. V. Yousefi, D. Mohebbi-Kalhari, A. Samimi, *Electrochim. Acta* **283** (2018) 234 (<https://doi.org/10.1016/j.electacta.2018.06.173>)
78. F. J. Hernandez-Fernandez, A. de los Rios, F. Mateo-Ramirez, M. D. Juarez, L. J. Lozano-Blanco, C. Godinez, *Sep. Purif. Technol.* **160** (2016) 51 (<https://doi.org/10.1016/j.seppur.2015.12.047>)

79. V. Kumar, S. Mondal, A. Nandy, P. P. Kundu, *Biochem. Eng. J.* **111** (2016) 34 (<https://doi.org/10.1016/j.bej.2016.03.003>)
80. S. Angioni, L. Millia, G. Bruni, D. Ravelli, P. Mustarelli, E. Quartarone, *J. Power Sources* **348** (2017) 57 (<https://doi.org/10.1016/j.jpowsour.2017.02.084>)
81. A. Sivasankaran, D. Sangeetha, Y.H. Ahn, *Chem. Eng. J.* **289** (2016) 442 (<https://doi.org/10.1016/j.cej.2015.12.095>)
82. C. Li, L. Wang, X. D. Wang, M. X. Kong, Q. Zhang, G. Y. Li, *J. Membrane Sci.* **527** (2017) 35 (<https://doi.org/10.1016/j.memsci.2016.12.065>).