# Hydrogels Used in Microbial Electrochemical Technologies

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Hydrogel materials have been used extensively in microbial electrochemical technology (MET) and sensor development due to their high biocompatibility and low toxicity. With an increasing demand for sensors across different sectors, it is crucial to understand the current state within the sectors of hydrogel METs and sensors.

Keywords: microbial electrochemical technology ; microbial sensors ; microbial fuel cells

## 1. Introduction

Microbial electrochemical technology (MET) is a fast-expanding field of research that utilises the metabolism of electrogenic microbes to catalyse oxidation and reduction reactions that occur in the anode and cathode [1][2]. The electrogenic microorganisms are able to release electrons through a variety of electron transfer methods and the electron is then passed from the anode to the cathode to produce an electrical output. MET is an overlap of a variety of research areas including microbiology and electrochemistry, material sciences, environmental and electrical engineering, etc. [3][4]. Its ability to sustainably utilise and convert a wide range of products in any form (solid, liquid, or gas) into useful products such as electricity and biofuels makes it highly applicable in a wide variety of research fields [5].

Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are the most typical METs widely used for wastewater treatment and green energy production. In recent literature, they have garnered significant interest in the sensor industry due to their versatile biosensing properties and ability to use microorganisms as a biocatalyst [6]. They have been developed as the sensor detecting organic matters (e.g., biological oxygen demand—BOD [7]), nutrients (e.g., nitrate ions [8]), toxicants (e.g., heavy metals [9][10]) in water, wastewater, soil, and human fluid. Additionally, the ability of MFCs and MECs to act as energy sources demonstrates the potential of these technologies to act as alternative green power supplies for sensors [11].

Hydrogels have great advantages when applied to METs and sensor technology development. For instance, a typical biosensor consists of four parts: the analyte, the analyte binding substrate, the transducer, and the data processor [12]. The stability and sensitivity of a biosensor are crucial during its application. Hydrogels are composed of a network of three-dimensional crosslinked polymers that are able to absorb large amounts of liquid [13]. They have a range of unique properties including swelling behaviour, biocompatibility, non-toxicity, porous structure, and self-healing [14], which makes them extremely versatile and suitable for improving the stability and sensitivity of the sensor. Hydrogel networks can either be chemically or physically crosslinked, ensuring structural stability during water absorption [15]. This allows the hydrogel to immobilise the biological substrate as well as create a microenvironment in which the analyte can be confined, thus improving the sensitivity [16]. These properties make hydrogels extremely suitable for electrochemical biosensing applications and development [17].

## 2. Hydrogels for Microbial Immobilisation

In the last ten years, hydrogels have become a common material used for microbial immobilisation, which is crucial for METs [15]. The highly porous structure and rigid matrix provide a stable environment, protecting microbes from environmental fluctuations [18]. This benign environment can suppress outside noise, thereby improving sensing signals [19]. Singh et al. immobilised five strains of strontium-resistant bacteria into an acrylamide hydrogel polymer and found that the immobilised microbes had a higher rate of strontium removal efficiency [20].

Multiple researchers have used alginate [21], cellulose [22], gelatine [23], and silica [24] hydrogel to immobilise different bacterial species for a variety of sensing applications. *E. coli* is commonly used as the model organism in many studies

due to its fast growth and easy manipulation. Other popular bacterial species used include *S. oneidensis* [25], *G. oxidans* [26], and *Lactobacillus* sp. [27]. Microbes often have to be cultured just before use as they have been shown to lose their biological activity when placed in storage [28]. Immobilising *E. coli* in poly(vinyl alcohol) (PVA) hydrogels showed exceptional biological activity even after 40 days of storage [29].

Electrochemical sensors often employ electrogenic microbes for sensing as the microbial metabolism can convert chemical energy to electrical energy, forgoing the need for transducers [30]. The electrogenic microbes are often found in consortiums in the form of stable biofilms; however, this can decrease the selectivity of the species. Single species are beneficial as organic consumption is directly linked to the voltage output; however, single-species biofilm is rarely seen in nature and tends to be unstable [31]. Hydrogels can act as an artificial matrix, allowing for single species to be embedded. Kaiser et al. embedded *S. oneidensis* into a PVA hydrogel anode and compared the electrochemical performance to an anode only containing a natural biofilm [32]. The hydrogel-embedded anode showed an improved voltage output. For highly electrogenic pure culture microbes that lack the genes for biofilm formation, hydrogels can also improve immobilisation [33]. Evidently, hydrogel shows great advantages to carry and immobilise bacteria and benefit their performance.

# 3. Hydrogel-Based MFCs

## 3.1. Anode Hydrogels

### Conducting Polymer Hydrogels

Conducting polymer hydrogels (CPHs) are a class of materials that combine the high electrocatalytic activity of conductive polymers, with the porous structure of the hydrogel [34]. They are used in the anodes of MFCs as they can physically interact with cell membranes, aiding in the facilitation of electron transference [35]. The improved electrocatalytic activity reduces the electron transfer resistance, and the hydrogel encapsulates microbes in a buffered environment, thereby promoting metabolic activity [36].

Throughout literature, the fabrication of CPHs is commonly observed for anode fabrication [37][38][39]. Polyaniline (PANI) and polypyrrole (PPy) have often been used to modify anodes due to their good electrical conductivity and bioadhesive properties [35]. Cellulose hydrogels are often used in conjunction with PANI and PPy. In parallel studies, Mashkour et al. tested the power density of PANI-Bacterial cellulose (BC) and PPy-BC anode against a graphite plate anode [40]. The PANI-BC produced a maximum power density of 117.76 $mW/m^2$ whereas PPy-BC yielded a slightly higher power density of 136 $mW/m^2$. Further conductivity improvement was demonstrated by incorporating titanium dioxide into the PANI-BC construct [41].

The addition of multiple conductive materials into hydrogels has demonstrated an improvement in electrical conductivity. Szöllősi et al. created a composite hydrogel containing three electrically conductive materials (Alginate-PANI-titanium dioxide-graphite composite hydrogel) [42]. Although the addition of 0.05 g/mL of PANI and graphite separately yielded a ten-fold increase in conductivity, the addition of PANI and graphite together enhanced the conductivity 105-fold. However, increasing the carbon materials results in the collapse of the gel matrix. A compromise concentration of 0.02 g/mL and 0.05 g/mL of PANI and graphite respectively demonstrated improved conductivity and was able to run continuously for 7 days. Wang et al. created an alginate, PANI, and carbon brush (CB) electrode to monitor chemical oxygen demand (COD) removal [43]. The MFC resulted in a power output of 515 $mW/m^2$, 1.5 times greater than the bare anode. Wang et al. further constructed PPy, carboxymethyl cellulose (CMC), and carbon nanotubes (CNT) construct on a CB. The power density output of 2970 $mW/m^2$ was 4.34 times greater than the bare anode. This large difference in comparison to the PANI study would mainly be due to the addition of CNTs [44].

Mixing two types of conductive polymers has been shown to also increase the power density. PANI and PPy hydrogel anodes have been shown to have similar power densities (2737.12 and 2859.53 $mW/m^3$); however, the PANI-PPy hybrid hydrogel anode had a noticeably higher power density (4413.03 $mW/m^3$). Further addition of CNT and $Fe_3O_4$ into the composite reduced internal resistance improving power density [45].

### Carbon Composite Hydrogels

CNTs are a class of nanostructures that are increasingly being applied to the anode of MFC due to their ability to improve the electrocatalytic activity of microbes [46]. In 2014, Lui et al. fabricated a CNT-chitosan hydrogel anode by electrodepositing CNT–Chitosan onto a carbon paper anode [47]. The CNT was able to improve the power and current density by allowing direct electron transference between the cytochrome enzyme and the anode. Further improvement of

MFC performance can be achieved by incorporating CNT into a CPH. A graphene oxide (GO), CNT, and Poly N-Isopropylacrylamide (PNIPAM) hydrogel anode showed a 100% increase in power and current densities [48]. PPy is another common conductive polymer commonly forming a composite with CNT. Examples in the literature include the production of a PPy-CNT hydrogel [46], and PPy, CMC and nitrogen-doped CNT hydrogel [49], both showing improved power output.

GO is another common material used within electrodes due to its hydrophilic nature and large surface area, supporting microbial adhesion and growth. GO is not a conductive material; however, it can be reduced by some species of microbes and act as a conductor [50]. According to a study by Yoshida et al., the growth of certain electrogenic microbial species has been linked to GO reduction, and the resulting structure is an reduced graphene oxide (rGO) microbial complex [51]. This rGO hydrogel complex has since been used for electricity recovery from dialysis wastewater using MFCs, however, the current output was lower than expected [52]. This is explained by incomplete GO reduction, therefore longer incubation between GO and the microbial species is required [53].

### 3.2. Cathode Hydrogels

Although a large body of hydrogel-based MFC research is dedicated to improving the microbe–anode interactions and electron transfer efficiency, some studies have applied hydrogels to the cathode of MFC to improve oxygen reduction reactions (ORRs). ORRs are the reduction half-reaction that occurs at the cathode, reducing oxygen to water or hydrogen peroxides [54]. ORR catalysts are often used to improve the slow and complex ORR kinetics that occur in traditional air cathodes, directly effecting electric energy production [55]. Current ORR catalysts are expensive and scarce, with some disrupting oxygen and ion transfer. Hydrogel-derived cathodes have been fabricated in multiple studies to improve ORR performance.

Li et al. synthesised a microalgae hydrogel whereby *Chlorella pyrenoidosa*, conductive polyacrylonitrile fibre, and agar gel were applied to the cathode [56]. A 33% increase in maximum power density was produced in comparison to the traditional Pt electrode. This cathode however was limited by carbonate precipitation after prolonged operations. A tofu gel produced from soybeans was mixed with nitrogen and iron co-doped carbon to produce an ORR electrocatalyst [57]. They showed a maximum power output increase of 30.62% in comparison to the Pt electrode. The highest power density MFC was synthesised by Yang et al., whereby a nitrogen and iron chitosan gel was applied to activated carbon support [58]. The MFC had a shorter running time in comparison to the tofu gel and was slightly more expensive to fabricate than the other hydrogels.

### 3.3. Membrane, Separator, and Electrolyte Hydrogels

Nafion or non-fluorinated polymers are traditionally used as the proton exchange membrane of MFCs due to their high proton conductivity, thermal and mechanical stability, and durability in the hydrated state. The high cost of these non-fluorinated membranes has resulted in their replacement with cheaper alternatives such as polyvinyl alcohol (PVA) [59]. The hydrogel form of PVA (PVA-H) can undergo repeated cycles of freezing and thawing to create an elastomer membrane [60]. The membrane showed excellent proton exchange, and when combined with the cathode to form an electrode assembly, further improved electricity production [59].

PVA-H has only been applied to air cathodes and the MFCs are used to remove or degrade toxins from water sources. Chang et al. created a tubular MFC with the PVA-H PEM to remove benzene from ground water, while Wu et al. created a waterfall MFC to remove organics from molasses wastewater [60][61]. A similar application to remove azo dye was also conducted in 2017 [62]. Insufficient water uptake and retention by PVA-H can limit the proton transference ability of the material. In order to solve this, Liu et al. incorporated a water-retaining clay into the PVA-H, improving the proton conductivity by 2.87 times compared to the PVA-H MFC [63].

Evaporation is a common limitation in many air cathodes, especially miniature MFCs, resulting in unstable power generation [64]. Hydrogel polymers often contain hydrophilic functional groups; therefore when water evaporates, the internal pressure is reduced allowing the substrate to be pulled into the hydrogel. This phenomenon has been exploited to maintain ion transport in a horizontal air cathode design [65], to improve the contact between the ion exchange membrane in an MEA air cathode [66], and to create an auto feeding MFC that is able to draw up substrates mimicking transpiration [67]. Hydrogel electrolytes can be used to improve cathode potential without disrupting ion exchange.

## 4. Hydrogel-Based MECs

Hydrogels have also been used in MEC research for microbial immobilisation. Lescano et al. aimed to improve the efficiency of bioelectrochemical systems by improving the bacteria loading capacity of electrodes [68]. Graphene electrodes have been increasingly used due to their conductivity, high mechanical strength, and stability. However, the 2D structure limits bacterial attachments. Lescano et al. immobilised the electrogenic bacteria, *Geobacter sulfurreducens*, in a graphene hydrogel. The graphene hydrogel electrode resulted in a three-time increase in current density in comparison to that of the bare graphene electrode. The SEM images of the hydrogel showed large pore structures with dense microbial growth on the electrodes.

Gandu et al. on the other hand utilised hydrogels to isolate exoelectrogens from non-exoelectrogens, reducing competition for nutrients and resources [69]. The *Geobacter sulfurreducens* bacteria were immobilised in an alginate and chitosan hydrogel and the current density, COD removal, and hydrogen production was measured. The MEC systems were treated with acetate and wastewater, one containing no additional bacteria and the other containing free-growing microbes. The study found that the non-immobilised system performed better when fed with acetate; however, this performance decreased significantly when the analytes were switched to wastewater. The opposite occurred for the hydrogel-immobilised MECs. Genetic analysis of the communities showed that the hydrogel was able to maintain the community composition of the exoelectrogens, and protect it from external competitors [70].

Modification to improve the microbe-electrode interaction has been conducted on both MECs and MFCs [71]. Electrode and microbial modifications, cell immobilisation, and electrode material selection have been extensively researched [72][73][74]. Although hydrogels are not commonly used within MEC research, other microbe immobilisation methods are used [75]. Dubrovin et al. for example looked at encapsulating the microbial anode in a microfiltration membrane and Rozenfield et al. utilised a dialysis bag for the encapsulation [69][76].

Aerogels are macroporous versions of hydrogels that are also used in microbial entrapment of MECs. They are prepared via the sol–gel process followed by supercritical drying to remove all the liquid of the gel and replace it with air [77]. The following gel is extremely lightweight, highly macroporous, has good thermal conductivity, large surface area, and low density [78]. Hou et al. created an aerogel anode from Molybdenum disulphide (MoS2) and nitrogen-doped graphene (NG) [79]. The hybrid $MoS_2$/NG has excellent electrocatalytic activity as well as good conductivity. By changing the structure from 2D to 3D aerogel, the porosity and surface area of the gel increased, further improving electrocatalytic activity. Another paper experimented on carbon aerogels and found that the hydrogen production was five times higher than that of the carbon cloth control [80]. The large surface area and large pores can promote greater microbial attachment, extracellular electron transfer, and electrocatalytic activity and make it a popular material for MECs.

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## References


1. Casula, E.; Mascia, M.; De Gioannis, G.; Di Lorenzo, M.; Isipato, M.; Muntoni, A.; Spiga, D. Modelling Miniature Microbi al Fuel Cells with Three-dimensional Anodes. E3S Web Conf. 2022, 334, 08005.
2. Hu, Y.; Rehnlund, D.; Klein, E.; Gescher, J.; Niemeyer, C.M. Cultivation of Exoelectrogenic Bacteria in Conductive DNA Nanocomposite Hydrogels Yields a Programmable Biohybrid Materials System. ACS Appl. Mater. Interfaces 2020, 12, 14806–14813.
3. Aulenta, F.; Puig, S.; Harnisch, F. Microbial electrochemical technologies: Maturing but not mature. Microb. Biotechnol. 2018, 11, 18–19.
4. Li, D.; Shi, Y.; Gao, F.; Yang, L.; Li, S.; Xiao, L. Understanding the current plummeting phenomenon in microbial fuel cel ls (MFCs). J. Water Process Eng. 2021, 40, 101984.
5. Mashkour, M.; Rahimnejad, M.; Mashkour, M.; Bakeri, G.; Luque, R.; Oh, S.-E. Application of Wet Nanostructured Bact erial Cellulose as a Novel Hydrogel Bioanode for Microbial Fuel Cells. ChemElectroChem 2017, 4, 648–654.
6. Wang, J.; Zhao, S.; Kakade, A.; Kulshreshtha, S.; Liu, P.; Li, X. A Review on Microbial Electrocatalysis Systems Couple d with Membrane Bioreactor to Improve Wastewater Treatment. Microorganisms 2019, 7, 372.
7. Pham, T.H.; Jang, J.K.; Chang, I.S.; Kim, B. Improvement of Cathode Reaction of a Mediatorless Microbial Fuel Cell. J. Microbiol. Biotechnol. 2004, 14, 324–329.
8. Wang, D.; Liang, P.; Jiang, Y.; Liu, P.; Miao, B.; Hao, W.; Huang, X. Open external circuit for microbial fuel cell sensor to monitor the nitrate in aquatic environment. Biosens. Bioelectron. 2018, 111, 97–101.

9. Yu, D.; Bai, L.; Zhai, J.; Wang, Y.; Dong, S. Toxicity detection in water containing heavy metal ions with a self-powered microbial fuel cell-based biosensor. Talanta 2017, 168, 210–216.
10. Liu, L.; Lu, Y.; Zhong, W.; Meng, L.; Deng, H. On-line monitoring of repeated copper pollutions using sediment microbial fuel cell based sensors in the field environment. Sci. Total Environ. 2020, 748, 141544.
11. Ivars-Barceló, F.; Zuliani, A.; Fallah, M.; Mashkour, M.; Rahimnejad, M.; Luque, R. Novel applications of microbial fuel c ells in sensors and biosensors. Appl. Sci. 2018, 8, 1184.
12. Chalklen, T.; Jing, Q.; Kar-Narayan, S. Biosensors Based on Mechanical and Electrical Detection Techniques. Sensors 2020, 20, 5605.
13. Adorinni, S.; Rozhin, P.; Marchesan, S. Smart Hydrogels Meet Carbon Nanomaterials for New Frontiers in Medicine. Bi omedicines 2021, 9, 570.
14. Sánchez-Cid, P.; Jiménez-Rosado, M.; Romero, A.; Pérez-Puyana, V. Novel Trends in Hydrogel Development for Biom edical Applications: A Review. Polymers 2022, 14, 3023.
15. Herrmann, A.; Haag, R.; Schedler, U. Hydrogels and Their Role in Biosensing Applications. Adv. Healthc. Mater. 2021, 10, 2100062.
16. Fu, L.; Yu, A.; Lai, G. Conductive Hydrogel-Based Electrochemical Sensor: A Soft Platform for Capturing Analyte. Chem osensors 2021, 9, 282.
17. Tavakoli, J.; Tang, Y. Hydrogel Based Sensors for Biomedical Applications: An Updated Review. Polymers 2017, 9, 364.
18. Hasan, S.; Kouzani, A.Z.; Adams, S.; Long, J.; Mahmud, M.A.P. Recent progress in hydrogel-based sensors and energ y harvesters. Sens. Actuators A Phys. 2022, 335, 113382.
19. Bae, J.; Park, J.; Kim, S.; Cho, H.; Kim, H.J.; Park, S.; Shin, D.-S. Tailored hydrogels for biosensor applications. J. Ind. Eng. Chem. 2020, 89, 1–12.
20. Singh, R.; Shitiz, K.; Singh, A. Immobilization of Bacterial Cells in Hydrogels Prepared by Gamma Irradiation for Biorem oval of Strontium Ions. Water Air Pollut. 2020, 231, 7.
21. Wasito, H.; Fatoni, A.; Hermawan, D.; Susilowati, S.S. Immobilized bacterial biosensor for rapid and effective monitorin g of acute toxicity in water. Ecotoxicol. Environ. Saf. 2019, 170, 205–209.
22. Drachuk, I.; Harbaugh, S.; Geryak, R.; Kaplan, D.L.; Tsukruk, V.V.; Kelley-Loughnane, N. Immobilization of Recombina nt E. coli Cells in a Bacterial Cellulose–Silk Composite Matrix to Preserve Biological Function. ACS Biomater. Sci. Eng. 2017, 3, 2278–2292.
23. Ebrahimi, E.; Yazdian, F.; Amoabediny, G.; Shariati, M.R.; Janfada, B.; Saber, M. A microbial biosensor for hydrogen sul fide monitoring based on potentiometry. Process Biochem. 2014, 49, 1393–1401.
24. Sakkos, J.K.; Kieffer, D.P.; Mutlu, B.R.; Wackett, L.P.; Aksan, A. Engineering of a silica encapsulation platform for hydro carbon degradation using Pseudomonas sp. NCIB 9816-4. Biotechnol. Bioeng. 2016, 113, 513–521.
25. Song, R.-B.; Yan, K.; Lin, Z.-Q.; Chye Loo, J.S.; Pan, L.-J.; Zhang, Q.; Zhang, J.-R.; Zhu, J.-J. Inkjet-printed porous pol yaniline gel as an efficient anode for microbial fuel cells. J. Mater. Chem. A 2016, 4, 14555–14559.
26. Schenkmayerová, A.; Bertóková, A.; Šefčovičová, J.; Štefuca, V.; Bučko, M.; Vikartovská, A.; Gemeiner, P.; Tkáč, J.; Ka trlík, J. Whole-cell Gluconobacter oxydans biosensor for 2-phenylethanol biooxidation monitoring. Anal. Chim. Acta 201 5, 854, 140–144.
27. Sagiroglu, A.; Paluzar, H.; Ozcan, H.M.; Okten, S.; Sen, B. A novel biosensor based on Lactobacillus acidophilus for de termination of phenolic compounds in milk products and wastewater. Prep. Biochem. Biotechnol. 2011, 41, 321–336.
28. Futra, D.; Heng, L.; Surif, S.; Ahmad, A.; Ling, T. Microencapsulated Aliivibrio fischeri in Alginate Microspheres for Monit oring Heavy Metal Toxicity in Environmental Waters. Sensors 2014, 14, 23248–23268.
29. Liu, C.; Xu, Y.; Han, X.; Chang, X. The fabrication and the use of immobilized cells as test organisms in a ferricyanide-b ased toxicity biosensor. Environ. Toxicol. Chem. 2018, 37, 329–335.
30. Hassan, R.Y.A.; Febbraio, F.; Andreescu, S. Microbial Electrochemical Systems: Principles, Construction and Biosensin g Applications. Sensors 2021, 21, 1279.
31. Berlanga, M.; Guerrero, R. Living together in biofilms: The microbial cell factory and its biotechnological implications. Mi crob. Cell Factories 2016, 15, 165.
32. Kaiser, P.; Reich, S.; Leykam, D.; Willert-Porada, M.; Greiner, A.; Freitag, R. Electrogenic Single-Species Biocomposite s as Anodes for Microbial Fuel Cells. Macromol. Biosci. 2017, 17, 1600442.
33. Suravaram, S.K.; Smith, D.K.; Parkin, A.; Chechik, V. Conductive Gels Based on Modified Agarose Embedded with Gol d Nanoparticles and their Application as a Conducting Support for Shewanella Oneidensis MR-1. ChemElectroChem 2

019, 6, 5876–5879.

34. Tang, X.; Li, H.; Du, Z.; Wang, W.; Ng, H.Y. Conductive polypyrrole hydrogels and carbon nanotubes composite as an a node for microbial fuel cells. RSC Adv. 2015, 5, 50968–50974.
35. Qi, L.J.; Wu, J.S.; Chen, Y.; Wen, Q.; Xu, H.T.; Wang, Y.Y. Shape-controllable binderless self-supporting hydrogel anod e for microbial fuel cells. Renew. Energy 2020, 156, 1325–1335.
36. Hindatu, Y.; Annuar, M.S.M.; Gumel, A.M. Mini-review: Anode modification for improved performance of microbial fuel c ell. Renew. Sustain. Energy Rev. 2017, 73, 236–248.
37. Liao, Y.H.; Liang, K.; Ren, Y.R.; Huang, X.B. Fabrication of SiOx-G/PAA-PANi/Graphene Composite With Special Cross -Doped Conductive Hydrogels as Anode Materials for Lithium Ion Batteries. Front. Chem. 2020, 8, 96.
38. Liu, B.R.; Soares, P.; Checkles, C.; Zhao, Y.; Yu, G.H. Three-Dimensional Hierarchical Ternary Nanostructures for High-Performance Li-Ion Battery Anodes. Nano Lett. 2013, 13, 3414–3419.
39. Shi, Y.; Wang, M.; Ma, C.B.; Wang, Y.Q.; Li, X.P.; Yu, G.H. A Conductive Self-Healing Hybrid Gel Enabled by Metal-Liga nd Supramolecule and Nanostructured Conductive Polymer. Nano Lett. 2015, 15, 6276–6281.
40. Mashkour, M.; Rahimnejad, M.; Mashkour, M. Bacterial cellulose-polyaniline nano-biocomposite: A porous media hydro gel bioanode enhancing the performance of microbial fuel cell. J. Power Sources 2016, 325, 322–328.
41. Truong, D.H.; Dam, M.S.; Bujna, E.; Rezessy-Szabo, J.; Farkas, C.; Vi, V.N.H.; Csernus, O.; Nguyen, V.D.; Gathergoo d, N.; Friedrich, L.; et al. In situ fabrication of electrically conducting bacterial cellulose-polyaniline-titanium-dioxide com posites with the immobilization of Shewanella xiamenensis and its application as bioanode in microbial fuel cell. Fuel 2 021, 285, 119259.
42. Szöllősi, A.; Hoschke, Á.; Rezessy-Szabó, J.M.; Bujna, E.; Kun, S.; Nguyen, Q.D. Formation of novel hydrogel bio-anod e by immobilization of biocatalyst in alginate/polyaniline/titanium-dioxide/graphite composites and its electrical performa nce. Chemosphere 2017, 174, 58–65.
43. Wang, Y.; Wen, Q.; Chen, Y.; Zheng, H.; Wang, S. Enhanced performance of microbial fuel cell with polyaniline/sodium alginate/carbon brush hydrogel bioanode and removal of COD. Energy 2020, 202, 117780.
44. Wang, Y.; Wen, Q.; Chen, Y.; Li, W. Conductive polypyrrole-carboxymethyl cellulose-titanium nitride/carbon brush hydro gels as bioanodes for enhanced energy output in microbial fuel cells. Energy 2020, 204, 117942.
45. Xu, H.; Du, Y.; Chen, Y.; Wen, Q.; Lin, C.; Zheng, J.; Qiu, Z. Electricity generation in simulated benthic microbial fuel cel l with conductive polyaniline-polypyrole composite hydrogel anode. Renew. Energy 2022, 183, 242–250.
46. Zou, Y.; Xiang, C.; Yang, L.; Sun, L.-X.; Xu, F.; Cao, Z. A mediatorless microbial fuel cell using polypyrrole coated carbo n nanotubes composite as anode material. Int. J. Hydrog. Energy 2008, 33, 4856–4862.
47. Liu, X.W.; Huang, Y.X.; Sun, X.F.; Sheng, G.P.; Zhao, F.; Wang, S.G.; Yu, H.Q. Conductive Carbon Nanotube Hydrogel as a Bioanode for Enhanced Microbial Electrocatalysis. Acs Appl. Mater. Interfaces 2014, 6, 8158–8164.
48. Kumar, G.G.; Hashmi, S.; Karthikeyan, C.; GhavamiNejad, A.; Vatankhah-Varnoosfaderani, M.; Stadler, F.J. Graphene oxide/carbon nanotube composite hydrogels-versatile materials for microbial fuel cell applications. Macromol. Rapid Co mmun. 2014, 35, 1861–1865.
49. Wang, Y.Y.; Pan, X.; Chen, Y.; Wen, Q.; Lin, C.G.; Zheng, J.Y.; Li, W.; Xu, H.T.; Qi, L.J. A 3D porous nitrogen-doped car bon nanotube sponge anode modified with polypyrrole and carboxymethyl cellulose for high-performance microbial fuel cells. J. Appl. Electrochem. 2020, 50, 1281–1290.
50. Salas, E.C.; Sun, Z.; Lüttge, A.; Tour, J.M. Reduction of graphene oxide via bacterial respiration. ACS Nano 2010, 4, 48 52–4856.
51. Yoshida, N.; Miyata, Y.; Doi, K.; Goto, Y.; Nagao, Y.; Tero, R.; Hiraishi, A. Graphene oxide-dependent growth and self-a ggregation into a hydrogel complex of exoelectrogenic bacteria. Sci. Rep. 2016, 6, 21867.
52. Yoshida, N.; Miyata, Y.; Mugita, A.; Iida, K. Electricity Recovery from Municipal Sewage Wastewater Using a Hydrogel Complex Composed of Microbially Reduced Graphene Oxide and Sludge. Materials 2016, 9, 742.
53. Goto, Y.; Yoshida, N. Microbially reduced graphene oxide shows efficient electricity ecovery from artificial dialysis waste water. J. Gen. Appl. Microbiol. 2017, 63, 165–171.
54. Ge, X.; Sumboja, A.; Wuu, D.; An, T.; Li, B.; Goh, F.W.T.; Hor, T.S.A.; Zong, Y.; Liu, Z. Oxygen Reduction in Alkaline Me dia: From Mechanisms to Recent Advances of Catalysts. ACS Catal. 2015, 5, 4643–4667.
55. Lu, M.; Guo, L.; Kharkwal, S.; Wu, H.n.; Ng, H.Y.; Li, S.F.Y. Manganese–polypyrrole–carbon nanotube, a new oxygen r eduction catalyst for air-cathode microbial fuel cells. J. Power Sources 2013, 221, 381–386.

56. Li, J.; Dong, Y.; Hu, L.; Zhang, Y.; Fu, Q.; Zhang, L.; Zhu, X.; Liao, Q. Microalgae hydrogel-derived monolithicfree-standi ng air cathode for microbial fuel cells: Tailoring the macroporous structure for enhanced bioelectricity generation. Rene w. Sustain. Energy Rev. 2022, 153, 111773.

57. Liu, J.; Wei, L.; Wang, H.; Lan, G.; Yang, H.; Shen, J. Biomass-derived N-doped porous activated carbon as a high-perf ormance and cost-effective pH-universal oxygen reduction catalyst in fuel cell. Int. J. Hydrog. Energy 2020, 45, 29308–29321.

58. Yang, W.; Wang, X.; Rossi, R.; Logan, B.E. Low-cost Fe–N–C catalyst derived from Fe (III)-chitosan hydrogel to enhan ce power production in microbial fuel cells. Chem. Eng. J. 2020, 380, 122522.

59. Liu, S.-H.; Wu, C.-H.; Lin, C.-W. Enhancement of bioelectricity generation for an air-cathode microbial fuel cell using pol yvinyl alcohol-membrane electrode assemblies. Biochem. Eng. J. 2017, 128, 210–217.

60. Wu, C.-H.; Liu, S.-H.; Chu, H.-L.; Li, Y.-C.; Lin, C.-W. Feasibility study of electricity generation and organics removal for a molasses wastewater by a waterfall-type microbial fuel cell. J. Taiwan Inst. Chem. Eng. 2017, 78, 150–156.

61. Chang, S.-H.; Wu, C.-H.; Wang, R.-C.; Lin, C.-W. Electricity production and benzene removal from groundwater using l ow-cost mini tubular microbial fuel cells in a monitoring well. J. Environ. Manag. 2017, 193, 551–557.

62. Lai, C.-Y.; Wu, C.-H.; Meng, C.-T.; Lin, C.-W. Decolorization of azo dye and generation of electricity by microbial fuel cel l with laccase-producing white-rot fungus on cathode. Appl. Energy 2017, 188, 392–398.

63. Liu, S.-H.; Chang, C.-M.; Lin, C.-W. Modifying proton exchange membrane in a microbial fuel cell by adding clay miner al to improve electricity generation without reducing removal of toluene. Biochem. Eng. J. 2018, 134, 101–107.

64. Cheng, S.; Liu, H.; Logan, B.E. Increased performance of single-chamber microbial fuel cells using an improved cathod e structure. Electrochem. Commun. 2006, 8, 489–494.

65. Li, Y.; Yang, W.; Liu, X.; Guan, W.; Zhang, E.; Shi, X.; Zhang, X.; Wang, X.; Mao, X. Diffusion-layer-free air cathode bas ed on ionic conductive hydrogel for microbial fuel cells. Sci. Total Environ. 2020, 743, 140836.

66. Kim, J.R.; Premier, G.C.; Hawkes, F.R.; Dinsdale, R.M.; Guwy, A.J. Development of a tubular microbial fuel cell (MFC) employing a membrane electrode assembly cathode. J. Power Sources 2009, 187, 393–399.

67. Wu, S.; Patil, S.A.; Chen, S. Auto-feeding microbial fuel cell inspired by transpiration of plants. Appl. Energy 2018, 225, 934–939.

68. Lescano, M.I.; Gasnier, A.; Pedano, M.L.; Sica, M.P.; Pasquevich, D.M.; Prados, M.B. Development and characterisatio n of self-assembled graphene hydrogel-based anodes for bioelectrochemical systems. RSC Adv. 2018, 8, 26755–2676 3.

69. Dubrovin, I.A.; Hirsch, L.O.; Rozenfeld, S.; Gandu, B.; Menashe, O.; Schechter, A.; Cahan, R. Hydrogen Production in Microbial Electrolysis Cells Based on Bacterial Anodes Encapsulated in a Small Bioreactor Platform. Microorganisms 2 022, 10, 1007.

70. Gandu, B.; Rozenfeld, S.; Ouaknin Hirsch, L.; Schechter, A.; Cahan, R. Immobilization of bacterial cells on carbon-cloth anode using alginate for hydrogen generation in a microbial electrolysis cell. J. Power Sources 2020, 455, 227986.

71. Yasri, N.; Roberts, E.P.L.; Gunasekaran, S. The electrochemical perspective of bioelectrocatalytic activities in microbial electrolysis and microbial fuel cells. Energy Rep. 2019, 5, 1116–1136.

72. Choudhury, P.; Prasad Uday, U.S.; Bandyopadhyay, T.K.; Ray, R.N.; Bhunia, B. Performance improvement of microbial fuel cell (MFC) using suitable electrode and Bioengineered organisms: A review. Bioengineered 2017, 8, 471–487.

73. Park, S.-G.; Rajesh, P.P.; Sim, Y.-U.; Jadhav, D.A.; Noori, M.T.; Kim, D.-H.; Al-Qaradawi, S.Y.; Yang, E.; Jang, J.-K.; Ch ae, K.-J. Addressing scale-up challenges and enhancement in performance of hydrogen-producing microbial electrolysi s cell through electrode modifications. Energy Rep. 2022, 8, 2726–2746.

74. Yuan, H.; He, Z. Graphene-modified electrodes for enhancing the performance of microbial fuel cells. Nanoscale 2015, 7, 7022–7029.

75. Wagner, R.C.; Porter-Gill, S.; Logan, B.E. Immobilization of anode-attached microbes in a microbial fuel cell. AMB Expr ess 2012, 2, 2.

76. Rozenfeld, S.; Gandu, B.; Hirsch, L.O.; Dubrovin, I.; Schechter, A.; Cahan, R. Hydrogen production in a semi-single-ch amber microbial electrolysis cell based on anode encapsulated in a dialysis bag. Int. J. Energy Res. 2021, 45, 19074–1 9088.

77. Gorgolis, G.; Galiotis, C. Graphene aerogels: A review. 2d Mater. 2017, 4, 032001.

78. Mao, J.; Iocozzia, J.; Huang, J.; Meng, K.; Lai, Y.; Lin, Z. Graphene aerogels for efficient energy storage and conversio n. Energy Environ. Sci. 2018, 11, 772–799.

79. Hou, Y.; Zhang, B.; Wen, Z.; Cui, S.; Guo, X.; He, Z.; Chen, J. A 3D hybrid of layered MoS2/nitrogen-doped graphene nanosheet aerogels: An effective catalyst for hydrogen evolution in microbial electrolysis cells. J. Mater. Chem. A 2014, 2, 13795–13800.
80. Wang, W.-K.; Tang, B.; Liu, J.; Shi, H.; Xu, Q.; Zhao, G. Self-supported microbial carbon aerogel bioelectrocatalytic anode promoting extracellular electron transfer for efficient hydrogen evolution. Electrochim. Acta 2019, 303, 268–274.