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Surface characteristics of electrodes in microbial electrolysis cells: a review on wastewater treatment

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Microbial electrolysis cells (MECs) are emerging as promising technologies for coupling wastewater treatment with renewable hydrogen production, but their efficiency hinges on electrode design. This review synthesizes 41 studies covering 55 electrode combinations, revealing how electrode composition and surface characteristics shape performance. Carbon-based anodes such as graphite felt and carbon cloth achieved chemical oxygen demand (COD) removal up to 95% and hydrogen production rates (HPR) between 0.1 and 45 m^3 of H_2 per m^3 of reactor per day. Metal-based cathodes, particularly stainless steel (SS304), yielded HPR values of up to 314 ± 17 m^3 of H_2 per m^3 of reactor per day with COD removal of 79 ± 4%. Modified electrodes incorporating nanoparticles and polymers further enhanced outcomes: Ni–Co–P coatings increased HPR nearly fivefold over bare metals, polymer-modified carbon felts doubled hydrogen yields and raised COD removal from 25% to >55%, and Cu/Ni nanocomposites achieved current densities of 226 A m^{-2} with COD removal above 75%. These results demonstrate that modified electrodes can rival platinum-based benchmarks at fabrication costs reduced by up to 50%. Despite these advances, significant challenges remain. Most studies employ simple substrates such as acetate, leaving performance under real wastewater conditions poorly understood. Key operational factors, including electrode spacing, microbial community engineering, and suppression of hydrogen-consuming pathways, are inconsistently addressed, and the long-term durability of non-noble metal cathodes under corrosive conditions is inadequately characterized. Looking forward, polymer–nanocomposite hybrids and three-dimensional electrode architectures represent promising innovations, combining high conductivity, biocompatibility, and surface area at lower cost. These strategies have already achieved COD removal above 80% and hydrogen yields approaching platinum controls, highlighting their potential to drive MECs toward scalable, cost-effective deployment in sustainable wastewater treatment and renewable energy production.

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Water impact

Conventional wastewater treatments are very energy-consuming, even more so with the growing world population, surfacing the need for alternative treatment techniques, such as microbial electrolysis cells, capable of both wastewater treatment and production of clean hydrogen-based fuels simultaneously. This review focuses on the compilation of optimal parameters and research gaps to move this novel technique from laboratory promise to real-world application.

1. Introduction

Globally, more than 359.4 billion m^3 of wastewater are produced every year, and nearly half (48%) is discharged untreated into the environment, posing severe risks to ecosystems and public health.[1] Conventional methods based on physical,[2,3] chemical[4,5] or biological[6,7] principles have advanced considerably, yet they remain energy-intensive and environmentally costly. The pressures of population growth and industrialization are driving unprecedented energy demand, much of it still met by fossil fuels, which accelerates global warming and biosphere degradation.[8]

Wastewater treatment plants (WWTPs) illustrate this paradox: designed to protect the environment, they contribute an estimated 3–4% of global greenhouse gas emissions. These emissions result from the high energy demands of aeration and pumping and the methane and nitrous oxide released during organic matter decomposition.

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Table 1 Average energy consumption for each step of a conventional wastewater treatment and their purpose

Process	Purpose	Range of energy consumption (kWh m^{-3})	Ref.
Primary treatment			
Raw sewage collection and pumping	Transport of raw sewage from houses and industries to WWTPs	0.003–0.04	12
Secondary treatment			
Sedimentation	Removal of heavier suspended solids and organic matter from wastewater through gravitational forces	0.008–0.01	12
Membrane bioreactor	Combine biological treatment with membrane filtration to achieve high-quality effluent by removing suspended solids, organic matter, and pathogens	0.49–1.5	13
Trickling filter	Remove organic pollutants and ammonia through microorganisms	0.18–0.42	12
Disinfection by UV light	Inactivate pathogenic microorganisms like bacteria, viruses, and cysts	0.021–0.066	12
Activated sludge	Biologically degrade organic pollutants and nutrients, reducing biological oxygen demand (BOD)	0.30–0.32	13
Tertiary treatment			
Oxidation ditch	Provide an aerobic environment for microorganisms to break down organic waste and convert it into a stable, harmless form	0.40–2.12	14
Nitrification	Convert toxic ammonia into less harmful nitrate, and prevent algal blooms and eutrophication	0.4–0.5	12
Phosphorus removal by microfiltration	Prevent eutrophication, algal blooms and oxygen depletion, and remove nutrient pollution	0.06–0.14	12

Table 1 summarizes the energy requirements of each treatment stage.[9]

Bioelectrochemical systems (BES) reduce the energy footprint of wastewater treatment by converting the chemical energy of organic matter directly into electricity or hydrogen.[1] In these systems, electroactive bacteria colonize electrodes and catalyze redox reactions, with anodic oxidation and cathodic reduction driving both pollutant degradation and energy recovery.[8,10] Common BES configurations include microbial fuel cells (MFCs) for bioelectricity, microbial electrolysis cells (MECs) for hydrogen, microbial desalination cells (MDCs) for water desalination, and microbial electrosynthesis (MES) for bio-based chemicals.[11]

Growing efforts to use renewable energy in WWTPs have drawn attention to MECs, which can produce high-purity hydrogen fuel at high efficiency.[1] Hydrogen (H_2) is an attractive alternative fuel, with a high energy density (120 MJ kg^{-1}) and the advantage of producing no GHGs at the point of use.

In an MEC, exoelectrogenic bacteria at the anode metabolize organic matter in an anaerobic environment, generating electrons, protons, and other metabolites through mechanisms like extracellular electron transfer (EET), which can occur *via* redox-active proteins, cytochromes, or conductive nanowires.[15] The electrons travel to the cathode, while protons migrate through the electrolyte, where they combine to form hydrogen.[16,17]

Several studies have focused on evaluating the performance of MECs by quantifying key parameters such as hydrogen production, coulombic efficiency (CE), and substrate degradation, although reported values vary widely with operational conditions.[1,18] Hydrogen production rates (HPRs) range from <1.0 L L^{-1} d^{-1} in pilot-scale systems treating real wastewater to >300 L L^{-1} d^{-1} in lab-scale reactors with optimized electrode configurations and substrates.[19–21] Importantly, these outputs are achieved with far lower energy input than conventional electrolysis, as MECs typically operate at 0.6–1.0 V, compared to conventional water electrolysis which requires 1.6–2.4 V.[20]

The efficiency of these systems is affected by numerous factors, including electrode materials, substrate type, and reactor design.[21–23] For instance, CE, which measures the conversion of substrate to current, is also highly variable. Values range from approximately 20% in pilot plants treating complex industrial wastewater to over 150% in single-chamber lab reactors where side reactions like hydrogen recycling can occur.[20,24] When treating wastewater, performance is also measured by organic matter degradation, with chemical oxygen demand (COD) removal efficiencies spanning from 40% to over 99% depending on the substrate complexity and hydraulic retention time.[20,25,26] Furthermore, MECs are effective for nutrient recovery, demonstrating phosphorus removal efficiencies of up to 98.6%.[26]

The choice of bacterial inoculum also influences performance in terms of organic matter degradation and electron generation: pure cultures are efficient with simple substrates, while mixed cultures can handle complex substrates but may also engage non-electrogenic pathways, reducing efficiency.[1,27,28] MECs can be designed as single-chamber or dual-chamber systems, with the latter providing higher hydrogen yields and better protection for the

microbial population, although at a higher construction cost.[29–31]

The material and surface characteristics of the anodes and cathodes are critical factors affecting the efficiency of MECs or any type of bioelectrochemical system.[29,32,33] The material of the electrodes affects energy conversion due to its role in linking the microbial and electrochemical processes. The desirable characteristics of materials used in anodes are good electrical conductivity, strong biocompatibility and low cost.[34,35] Additionally, detachment of the microorganisms from the flat surface of the anodes can cause a decrease in the efficiency of the system.[36,37] Moreover, thermodynamic potential loss by anodic and cathodic electrodes can account for almost 50% of the total potential loss of MECs,[38] and enhancing the performance of the electrodes by changing the configuration and material can drastically reduce the overall cost of the system, since the electrodes are responsible for up to 79% of the total construction cost of MECs.[39]

Some of the modifications studied to improve these characteristics include use of nanoparticles, carbon nanotubes, and conductive polymer deposition.[8,40] Also, 3D electrode configurations impact the surface area available for the attachment of the bacteria, as high surface area allows the attachment of more exoelectrogenic microorganisms, possibly increasing the hydrogen gas production and organic matter consumption. Some 3D configurations are being tested with variable results.[37]

Due to the importance of the anodes and cathodes in microbial electrolysis cells, this review aimed on compiling the recent advances in materials and configurations used to improve the electrodes' performance in MECs. A critical analysis of the knowledge and research gaps will also be provided.

To the best of our knowledge, the last comprehensive review dedicated to MEC electrodes was published prior to 2020 and primarily emphasized hydrogen production and scale-up feasibility. Since then, the field has advanced rapidly, with new studies exploring electrode surface modifications, alternative materials, and their dual role in hydrogen recovery and wastewater quality improvement. The absence of an updated, focused review highlights the need for this work.

The growth of MEC research in recent years underscores this urgency. As shown in Fig. S1, over 3000 MEC-related papers have been published in the last five years alone, an increase of 35% compared to the 2148 papers published in the preceding 17 years combined. This explosion of literature, while promising, also makes it difficult to discern consistent trends and identify the most effective strategies. A critical synthesis of these findings is therefore essential to guide future research, accelerate scale-up, and position MECs as a viable component of sustainable wastewater treatment and renewable energy generation.

2. Microbial electrolysis cells overview

Microbial electrolysis cells (MECs) are bioelectrochemical systems that extend anaerobic digestion processes to produce hydrogen and related products such as CH_4, H_2, and H_2O_2.[16,41] At the anode, exoelectrogenic bacteria oxidize organic matter under anaerobic conditions, releasing electrons and protons that are transferred to the cathode. Extracellular electron transfer (EET) occurs through cytochromes, redox-active proteins, conductive nanowires, or mineral-based electron shuttles.[15,42] Electrons flow through an external circuit while protons migrate through the electrolyte, recombining at the cathode to form molecular hydrogen.[16,17] The overall process couples substrate degradation with the hydrogen evolution reaction, as represented in the following reactions:[1]

$$\text{Anode: Aa} + \text{Bb} \rightarrow \text{Cc} + e^- + H^+ \quad (1)$$

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

The CH_4 and H_2 production can achieve rates up to 0.15 m^3 m^{-3} d^{-1} and 300 m^3 m^{-3} d^{-1}, respectively, which can be later used in internal combustion engines.[43] Methane is formed only in the presence of CO_2 and methanogens; if undesired, it can be suppressed by strategies such as cathode aeration, lowering pH, or reducing retention time. MEC performance is commonly evaluated through current generation, coulombic efficiency (CE), hydrogen recovery, and production rate, while wastewater quality parameters also serve as indicators of treatment effectiveness.[18,44,45]

Various substrates and wastewater have been used in MECs, aiming at the improvement of the H_2 production.[41] Acetate remains the most common substrate, as it is a natural fermentation product and readily utilized by exoelectrogenic microbes.[16,29,44]

The choice of inoculum also strongly affects outcomes: pure cultures perform predictably with simple substrates, whereas mixed cultures enable operation on complex feedstocks and under diverse conditions.[1,27,28] However, mixed communities also channel electrons into competing pathways such as methanogenesis and sulfate reduction, lowering CE.[1,31,46] Hengsbach and collaborators (2022) found that in equivalent experimental setups, a 3-fold higher methane production rate can be achieved in mixed cultures when compared to pure cultures.[47]

MECs can be configured as single- or dual-chamber systems (Fig. 1a and b). Single-chamber reactors are simpler but prone to hydrogen losses *via* methanogenesis and microbial inhibition from electrolysis intermediates.[30,48,49] Dual-chamber designs, separated by a proton exchange membrane (PEM), prevent oxygen crossover and can improve hydrogen yields by 10–30%, although at the cost of more complex construction.[50]

The following sections examine in detail how electrode configuration influences both hydrogen production and wastewater treatment performance in MECs and provide a critical synthesis and comparison of prior studies employing this technology.

3. Methodology

A systematic literature search was conducted in the ScienceDirect database using the terms "microbial electrolysis cell" AND

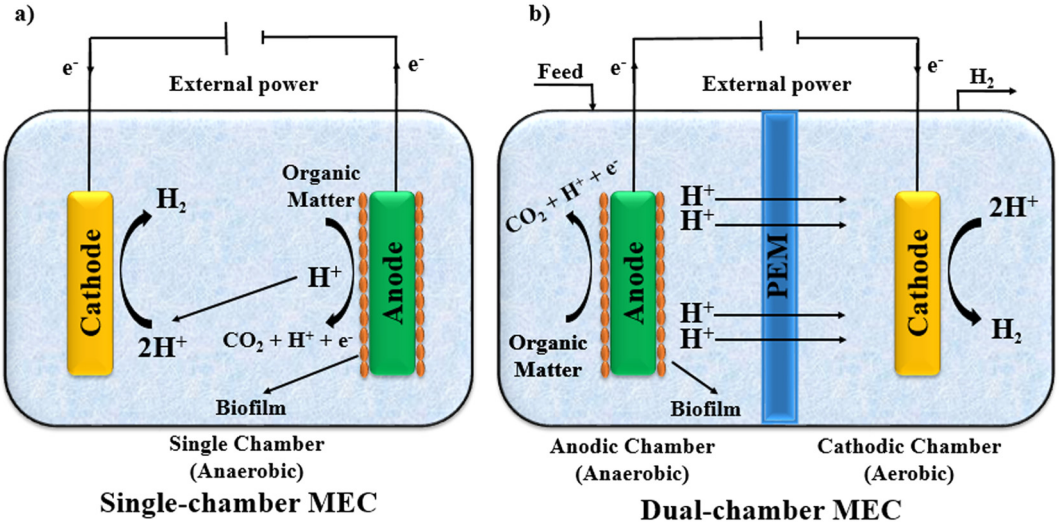

Fig. 1 Schematic diagram of two-chamber and single-chamber microbial electrolysis cells.

"electrode" OR "cathode" OR "anode." Only peer-reviewed journal articles in English were considered; review papers and book chapters were excluded. No date restrictions were applied. The search yielded 2057, 1857, and 1839 articles for the three respective queries. Results were sorted by relevance, and the top 20 papers from each query were screened. Studies were retained if they reported hydrogen or methane production rate (HPR), current density (CD), or COD/nutrient removal. After removing duplicates across queries, 41 unique articles were included, representing 55 electrode configurations. Of these, 60% examined plain electrodes and 40% investigated modified electrodes. A detailed summary of the selected studies is provided in Table S1.

4. Electrode configuration and its importance on the process efficiency

The choice of anode and cathode materials is critical in MEC design, as electrodes largely determine hydrogen production and organic matter degradation. Ideal electrodes combine high electrocatalytic activity, conductivity, current tolerance, corrosion resistance, mechanical stability, and large surface area.[29] The anode, supporting the biofilm, should have all the features of the cathode, and promote microbe–electrode interaction and be biocompatible with microbial growth.[1,51,52] Common electrode materials are described in detail in section 4.1. Table 2 summarizes representative studies including system configuration, microbial inoculum, applied potential, and performance indicators such as current density (CD), hydrogen production rate (HPR), and COD/nutrient removal. Other important parameters, such as electrocatalytic activity, corrosion resistance, hardness, surface area, and biocompatibility, are less frequently reported and are compiled in Table S2.

Electrode surfaces can be modified through various techniques to achieve desirable electrochemical, optical, and other properties without compromising system performance. Modifiable characteristics include porosity, surface roughness, micropillars, and surface charge distribution (hydrophobicity/hydrophilicity)[29,30] (Table 3).

4.1 Electrode material

4.1.1 Carbon-based electrodes. Several carbon materials have been reported: graphite blocks,[53] graphene felt,[21,54] graphite fiber brush,[45,55–57] carbon cloth,[19] biochar[58] and carbon felt.[32,59] Moreover, pyrolysed almond shells and crushed metallurgical coke have been used as electrodes in MECs.[60,61]

In conclusion, as shown in Table 2, graphene felt is the most conductive of the materials from all the studies, as it shows a CD from 10 to almost 300 times higher than the other materials, such as carbon cloth, graphite blocks and biochar, even when the potential added is very similar.[21,22,59] This material also shows promising results for COD removal, as high as 95% in sodium acetate and 94.1% in domestic wastewater.[54,62] Regarding hydrogen production, the combination of graphene felt for both the anode and the cathode is 25% more efficient than graphite blocks and carbon cloth with similar applied potential, even when using a more complex substrate such as synthetic wastewater.[21]

4.1.2 Metal-based electrodes. The most commonly used metals are stainless steel,[21,54] iron[21] and platinum.[57,63] Among these, one of the most prominent options are stainless steel (SS) electrodes due to their low cost, durable nature and good electrical conductivity of 2.5×10^6 S m^{-1}, which provides them a yield efficiency similar to that of more expensive metal-based materials, such as platinum electrodes.[29] For example, when using graphene felt as an anode and synthetic wastewater in a single chamber MEC, Posadas-Hernandéz and collaborators (2023) found a HPR of 0.193 m^3 m^{-3} d^{-1} with a SS304 mesh as the cathode, while Jwa *et al.* (2019) found a HPR of 0.180 m^3 m^{-3} d^{-1} with a Pt/C cathode.[21,62]

Recently, several transition metals such as nickel and molybdenum have been studied to be used as electrodes in MECs due to their high electrochemical activity, abundance,

Table 2 Compilation of studies using different materials as electrodes to produce hydrogen and methane on microbial electrolysis cells

Cathode	Anode	Configuration	Substrate	Biofilm	Yield	COD removal (%)	Applied potential (V)	Ref.
Carbon-based cathode/carbon-based anode								
Graphene felt	Graphene felt	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 17 ± 1.0 A m^{-2} HPR: 45 ± 8.0 m^3 m^{-3} d^{-1}	56 ± 3	0.8	21
Carbon felt	Carbon felt	Single-chamber	Synthetic wastewater	—	CD: 0.97 ± 0.3 A m^{-2} HPR: 0.116 ± 0.007 m^3 m^{-3} d^{-1}	—	0.8	22
Graphite block	Graphite block	Single-chamber	Cattle manure	*Methanoculleus* and *Candidatus methanogranum*	CD: 1.5 ± 0.05 A m^{-2} HPR: 0.15 ± 0.017 m^3 m^{-3} d^{-1}	18.3 ± 2.9	0.7	53
Spiral-wound woven wire mesh	Cylindrical porous graphite	Dual-chamber	Synthetic wastewater	—	—	Ni: 99.9	1.1	67
Biochar	Carbon felt	Single-chamber	Synthetic wastewater	—	CD: 16.8 ± 0.2 A m^{-2}	PO_4^{3-}–P: 28.8 ± 1 Ca: 40.3 ± 5	−0.6	58
Carbon cloth	Carbon cloth	Single-chamber	Lignocellulosic hydrolyzate	*Enterococcus spp.*	CD: 16.5 A m^{-2} HPR: 0.71 m^3 m^{-3} d^{-1}	—	1.36	19
Metal-based cathode/metal-based anode								
SS304 flat mesh 60	SS304 pleated mesh 60	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 91 ± 5.0 A m^{-2} HPR: 314 ± 17 m^3 m^{-3} d^{-1}	79 ± 4	0.8	21
Iron	SS304 flat mesh 60	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 56 ± 2.0 A m^{-2} HPR: 73 ± 10 m^3 m^{-3} d^{-1}	67 ± 1	0.8	21
SS304 flat mesh 60	SS304 flat mesh 60	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 13 ± 1.0 A m^{-2} HPR: 7.4 ± 1 m^3 m^{-3} d^{-1}	6 ± 1	0.8	21
Iron	SS304 pleated mesh 60	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 20 ± 2.0 A m^{-2} HPR: 9.0 ± 3.0 m^3 m^{-3} d^{-1}	48 ± 2	0.8	21
Metal-based cathode/carbon-based anode								
SS304 mesh	Graphene fiber brush	Dual-chamber	Sodium acetate	*G. sulfurreducens* strain DL1	CD: 1.05 A m^{-2} HPR: –	PO_4^{3-}–P: 92.03	0.9	45
Nickel foam	Carbon cloth	Single-chamber	Dairy wastewater	Domestic wastewater strains	CD: 24.0 A m^{-3} HPR: 0.03 m^3 m^{-3} d^{-1}	71 ± 5	0.9	24
Nickel foam	Carbon felt	Dual-chamber	Diluted industrial wastewater	*Geobacter, Bacteroides, Desulfovibrio and Klebsiella*	CD: 4.0 A m^{-2} HPR: 0.21 ± 0.01 m^3 m^{-3} d^{-1}	40	1.0	20
SS mesh	Carbon fiber brush	Single-chamber	Textile-dyeing wastewater	*Syntrophomonas, norank_f__ Syntrophobacteraceae, Geovibrio, Desulfovibrio, Psedomonas, Geobacter* and *Longilinea*	CD: 5.94 ± 0.03 A m^{-2}	74.75 ± 4.32	0.7	18

Table 2 *(continued)*

Cathode	Anode	Configuration	Substrate	Biofilm	Yield	COD removal (%)	Applied potential (V)	Ref.
SS304 flat mesh	Graphene felt	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 25 ± 2.0 A m^{-2} HPR: 193 ± 14 m^3 m^{-3} d^{-1}	76 ± 2	0.8	21
Iron	Graphene felt	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 280 ± 5.0 A m^{-2} HPR: 15 ± 4.0 m^3 m^{-3} d^{-1}	59 ± 3	0.8	21
$Ce_{0.1}$–Ni–Y	Carbon felt	Single-chamber	Synthetic wastewater	—	CD: 39.8 A m^{-2} HPR: 0.31 ± 0.013 m^3 m^{-3} d^{-1}	—	0.7	59
Stainless steel mesh	Graphite fiber brush	Single-chamber	Digestate from an anaerobic digester	—	HPR: 1.9 ± 0.04 m^3 m^{-3} d^{-1}	27.64 ± 1.78	1.07	57
SS304 mesh	Graphite felt	Single-chamber	Sodium acetate	*Proteobacteria* and *Firmicutes*	CD: 0.61 A m^{-3} HPR: 0.004 m^3 m^{-3} d^{-1}	95	0.5	54

low cost, and stability, aiming to enhance the hydrogen evolution reaction (HER) efficiency.[64,65] Amidst these, the nickel-based electrode usually shows better results due to its high density and possible smaller grain size with an electric conductivity of 14.3 S m^{-1}.[1,29,66]

As for the studies shown in Table 2, stainless steel seems to be the most popular choice for MECs, and their shape and distance can interfere with the CD and HPR of the system, as observed in the study performed by Posadas-Hernández *et al.* (2023), where by only replacing the cathode from a flat stainless steel mesh to a pleated stainless steel mesh, the CD increased 7 times, the volume of hydrogen produced increased 42 times, and the COD removal increased 13 times, even when maintaining all the other parameters the same, such as substrate, applied voltage and microbiota. An increase of these parameters was also found, although not as significant, when the authors replaced the flat mesh with an iron cathode instead.[21]

Carbon-based electrodes dominate MEC research, with 89% of studies employing either carbon–carbon pairs or carbon anodes coupled with metal cathodes, while only 11% use metal-based anodes. This trend likely reflects the higher biocompatibility of carbon materials. The relative biocompatibility of carbon and metal anodes remains poorly understood, representing a critical area for future studies.

4.1.3 Combination of metal and carbon-based electrodes. Beyond single-material electrodes, the majority of MEC studies focus on pairing carbon anodes with metal cathodes, a strategy that exploits the strong biocompatibility of carbon surfaces for biofilm formation together with the high conductivity and catalytic activity of metals at the cathode. In summary, stainless steel is the most used material for cathodes, while a variety of carbon-based materials are used for the anode. The highest CDs were achieved with iron cathode/graphene felt anode and stainless-steel mesh cathode/graphene felt with 280 ± 5.0 A m^{-2} and 323 ± 6.0 A m^{-2}, both higher than those of all the other studies included in this paper.[21]

Although a high CD does not always mean a higher hydrogen production, as shown by Posadas-Hernández *et al.* (2023), who used a flat stainless steel mesh as the cathode, resulting in a CD of 25 ± 2.0 A m^{-2} while producing 193 ± 14 L m^{-3} d^{-1} of H_2, and by using a pleated stainless steel mesh as the cathode, they observed a higher CD of 323 ± 6.0 A m^{-2} but a lower H_2 production of 48 ± 8.0 L m^{-3} d^{-1}. The same was observed in COD tests, where the electrode combination with a lower CD presented a COD removal of 76 ± 2%, whereas the combination with the highest CD presented a COD removal of only 56 ± 2%.[21]

Other cathode/anode combinations were shown, such as Mo_2N nanobelt/graphite fiber brush,[55] SS mesh/graphite fiber brush,[45] nickel foam/carbon cloth[24] and SS wire wool/carbon felt,[32] but none of these yielded as much hydrogen as the ones previously mentioned.

As shown in the table, studies combining carbon-based anodes with metal-based cathodes often adopt a more comprehensive approach, systematically testing how changes in individual parameters affect system efficiency, an essential consideration in BES research. In contrast, single-material studies tend to be narrower in scope and less detailed.

4.2 Electrode modification

Electrode modifications have been studied to improve the efficiency of the bioelectrochemical systems by making the

Table 3 Compilation of studies using nanocomposite modifiers on electrodes for the production of hydrogen on microbial electrolysis cells

Cathode	Anode	Configuration	Substrate	Biofilm	Yield	COD/nutrient removal (%)	Applied potential (V)	Ref.
Metal-modified electrodes								
Cu/Ni	Graphene felt	Single-chamber	Synthetic wastewater	*Paralicheniformis, Licheniformis, Sonorensis, Haynesii, Glycinifermentans* and *Anoxybacillus*	CD: 226 ± 4.0 A m^{-2} HPR: 223 ± 18 m^3 m^{-3} d^{-1}	76 ± 3	0.8	21
Pt/carbon cloth	Graphene felt	Single-chamber	Domestic wastewater	—	CD: 1.37 ± 0.10 A m^{-2} HPR: 0.92 ± 0.03 m^3 m^{-3} d^{-1}	94.1 ± 0.5	0.9	62
MoP/C	Carbon cloth	Single-chamber	Sodium acetate, glucose	—	CD: 34 ± 4.1 A m^{-2} HPR: 5.9 ± 1.4 m^3 m^{-3} d^{-1}	—	1.0	23
Pt/Ti mesh	Graphite felt	Single-chamber	Sodium acetate	*Proteobacteria*, *Bacteroidetes*, *Euryarchaeota*, *Actinobacteria*, and *Firmicutes*.	CD: 280 ± 15 A m^{-3} HPR: 4.59 ± 0.2 m^3 m^{-3} d^{-1}	~80	0.8	84
MoP/C	Carbon cloth	Single-chamber	Acetate with phosphate buffer	—	CD: 49.5 ± 5.3 A m^{-2} HPR: 39.8 ± 1.9 m^3 m^{-3} d^{-1}	—	1.01	87
ZIF-67/carbon cloth	Carbon cloth	Dual-chamber	Sucrose	SR10 strain	CD: 1.25 A m^{-2} HPR: 0.923 ± 0.04 m^3 m^{-3}	Sb removal: 92	0.8	85
Graphite block	NiMo/graphene	Dual-chamber	Sodium acetate	—	CD: 44.4 ± 0.9 A m^{-2} HPR: 81 ± 3.0 m^3 m^{-3} d^{-1}	—	- 0.86	82
MoS_2/nanocarbon	Carbon fiber bush	Dual-chamber	Urine wastewater	*Tissierella (Clostridia)* and *Bacteroidetes* taxa	CD: 7.15 ± 0.03 A m^{-2} HPR: 0.15 ± 0.002 m^3 m^{-3} d^{-1}	NH_3–N: 68.7 PO_4^{3-}–P: 98.6	0.9	26
Mo_2N nanobelt	Graphite fiber brush	Single-chamber	Synthetic wastewater	*Stenotrophomonas nitritireducens*, *Stenotrophomonas maltophilia*, and *Comamonas testosteroni*	CD: 4.19 A m^{-2} HPR: 0.39 ± 0.14 m^3 m^{-3} d^{-1}	—	0.77	55
Ni–Co–P/SS316	Graphite	Dual-chamber	Sugar industry wastewater	—	CD: 4.42 A $^{-}m^2$ HPR: 0.24 ± 0.005 m^3 m^{-3} d^{-1}	50	0.6	25
Ni–Co–P/Cu	Graphite	Dual-chamber	Sugar industry wastewater	—	CD: 4.32 A m^{-2} HPR: 0.21 ± 0.005 m^3 m^{-3} d^{-1}	47	0.6	25
Fe^{+2}/biochar	Carbon felt	Single-chamber	Synthetic wastewater	—	CD: 20.7 ± 0.8 A m^{-3}	PO_4^{3-}–P: 62.4 ± 3.5 Ca: 57.1 ± 2.4	0.8	58
Ru/CNTs	Carbon brush	Dual-chamber	Sodium acetate	—	CD: 17.13 A m^{-2} HPR: 0.167 m^3 m^{-2} d^{-1}	—	0.031	88
Pt/Ti mesh	Cylindrical graphite felt	Single-chamber	Acetate and butyrate	*Geobacter*, *Syntrophomonas* and	CD: 2.93 ± 0.03 A m^{-2}	Acetate: 95.3 ± 2.1	0.8	89

Table 3 *(continued)*

Cathode	Anode	Configuration	Substrate	Biofilm	Yield	COD/nutrient removal (%)	Applied potential (V)	Ref.
				Dysgonomonas	HPR: 6.26 ± 0.23 m^3 m^{-3} d^{-1}	Butyrate: 78.4 ± 3.6		
Pt/carbon felt	Carbon felt	Dual-chamber	Acetate	*Alpha-* and *Deltaproteobacteria*	CD: 2.3 A m^{-2} HPR: 0.37 ± 0.02 m^3 m^{-3} d^{-1}	—	1.0	90
CoNi@$CoFe_2O_4$/nickel foam	Carbon felt	Single-chamber	Bacterial solution and nutrient solution (1 : 4)	—	CD: 30.45 A m^{-2} HPR: 1.25 ± 0.06 m^3 m^{-3} d^{-1}	—	0.7	91
Pt/carbon cloth	Graphite fiber brush	Dual-chamber	Sodium acetate	—	CD: 5.7 ± 0.1 A m^{-2} H_2 production: 21.8 ± 2.2 mL	—	0.9	86
Pt/Ti	Graphite fiber brush	Dual-chamber	Sodium acetate	—	CD: 33.1 ± 2.3 A m^{-2} H_2 production: 23.0 ± 2.2 mL	—	0.9	86
CoP/nickel foam	Graphite brush	Dual-chamber	Sodium acetate	—	CD: 83 ± 4.0 A m^{-2} HPR: 0.22 ± 0.02 m^3 m^{-3} d^{-1}	—	0.7	92
Ni_2P/C	Graphite brush	Dual-chamber	Synthetic fermentation effluent	—	CD: 5.7 ± 0.1 A m^{-2} HPR: 0.3 ± 0.29 ± 0.04 m^3 m^{-3} d^{-1}	—	0.9	93
Pd/carbon cloth	Carbon brush	Dual-chamber	Sodium acetate	*S. oneidensis* MR-1	CD: 0.7 A m^{-2} HPR: 0.062 ± 0.002 m^3 m^{-3} d^{-1}	55.0 ± 1.3	0.8	83
MnO_2/carbon felt	Carbon felt	Dual-chamber	Glucose and Wolfe's solution	—	CD: 0.004 ± 0.0005 A m^{-2} HRP: 37.9 mmol L^{-1}	—	−1.15	70
Pt/C	Graphite brush	Dual-chamber	Sodium acetate	—	CD: 10.6 ± 0.3 A m^{-2} HPR: 1.2 ± 0.7 m^3 m^{-3} d^{-1}	—	0.45	56
Pt/C	Carbon felt	Dual-chamber	Sodium acetate	Anerobic sludge	HPR: 0.007 μmol cm^{-2} h^{-1}	—	0.3	63
Pt/C	3D porous carbon aerogel	Dual-chamber	Sodium acetate	Anerobic sludge	HPR: 0.37 μmol cm^{-2} h^{-1}	—	0.3	63
Pt/C	Graphite fiber brush	Single-chamber	Digestate from an anaerobic digester	—	HPR: 2.02 ± 0.03 m^3 m^{-3} d^{-1}	39.81 ± 2.34	1.07	57
Metal/carbon-modified electrodes								
Pt@rGO/carbon cloth	Graphite fiber brush	Single-chamber	Sodium acetate	—	CD: 7.8 A m^{-2} HPR: 2.25 m^3 m^{-2} d^{-1}	—	0.8	94

Table 3 *(continued)*

Cathode	Anode	Configuration	Substrate	Biofilm	Yield	COD/nutrient removal (%)	Applied potential (V)	Ref.
Mo_2C/NC-800	Carbon brush	Dual-chamber	Synthetic wastewater	—	CD: 20.2 A m^{-2} HPR: 0.17 m^3 m^{-2} d^{-1}	—	1.0	95
MoS_2–Cu–rGO/carbon paper	Carbon felt	Single-chamber	Nutrient solution	—	CD: 10.28 ± 0.40 A m^{-2} HPR: 0.449 ± 0.0027 m^3 m^{-3} d^{-1}		0.7	96

electrodes more suitable to the environment of the cells.[1] When electrodes have their surface changed, they are classified as chemically modified electrodes. The commonly used modification methods are electrochemical and substance adjustments (electrografting/electropolymerization), spray coating, and drop casting, that are based on physisorption, homogenous formation of multilayer thin film, and covalent modification.[29]

The electrochemical technique (Fig. 2) consists of the deposition of a dissolved chemical modifier on the surface of the electrode by an oxidation reaction, using cyclic voltammetry or controlled potential electrolysis.[68] This technique can be carried out in both aqueous and nonfluid medium.[69]

Anwer *et al.* (2023) used the electrochemical deposition method to develop a novel MnO_2-coated carbon felt cathode for microbial electroreduction of CO_2 to biofuels, and the results showed that the MnO_2-coated electrode offered higher electrode surface area and better electron transfer efficiency, resulting in an increase of the acetate consumption by 1.7-fold and making its use feasible for large-scale MECs.[70] In another study, this same modification technique was used to coat a nanocarbon electrode with MoS_2 nanoparticles, aiming for a better bioelectrochemical hydrogen production in a MEC while recycling urine. It was proved that the system produced a high amount of H_2 (0.152 ± 0.002 m^3 m^{-2} d^{-1}) and that the MoS_2-modified electrode could be a cost-effective alternative to the Pt cathode for renewable bioelectrochemical hydrogen production from urine.[26] Moreover, Yi and collaborators (2023) performed the electropolymerization of L-arginine on a carbon cloth electrode for its use in a microbial electrochemical system (MES). They observed that the modification increased the electrode electropositivity, increased the biofilm formation by 60%, increased the performance of the system by decreasing the charge transfer resistance by 62%, and enhanced the current generation by 76% when compared to the control electrode, which suggest the feasibility of MES electrode modification with *in situ* amino acid electropolymerization.[71]

In the case of the drop casting method (Fig. 3), the modifier particles are added to a suitable solvent and heated to the boiling point (except for metal oxide nanoparticles due to possible oxidation), and the suspension is dropped on the surface of the electrode. The particles present in the mix then become attached to the electrode surface once the solvent completely evaporates.[72]

Rani, Krishna and Yogalakshmi (2021) developed a Fe_3O_4 nanoparticles layered carbon electrode by the drop casting method to enhance the electrochemical performance of a MEC. They found high conductivity (58 S m^{-1}) and low bulk resistivity (0.4 kΩ) in the modified electrodes as well as a tenfold increase in current and power generation (15.2 mA cm^{-2} and 10.6 mW cm^{-2}, respectively) when compared to the non-modified electrodes, indicating an enhanced electrochemical performance. Hence, the results show that the modified electrodes helped in catalyzing the redox reaction considerably.[73] Hassan *et al.* (2017) also used the drop casting method to produce a graphene oxide sheet electrode modified with alumina nanocrystals to monitor microbial cell viability. The results showed an enhancement of electrocatalytic activity of the modified electrode which allowed

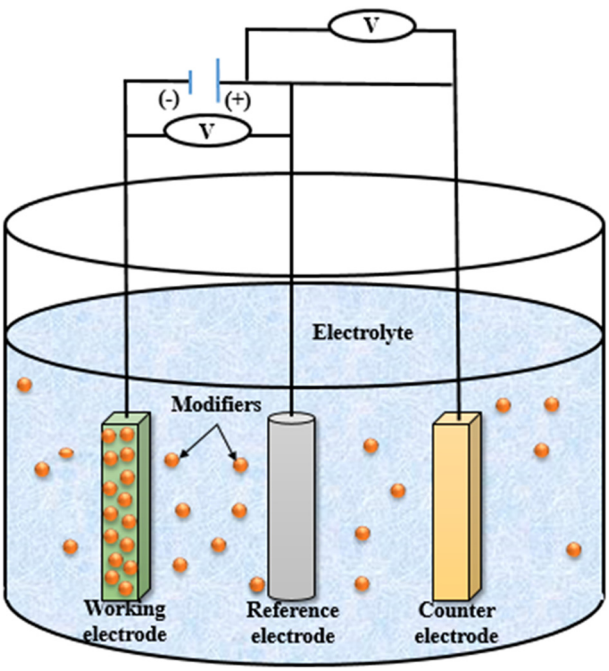

Fig. 2 Schematic diagram of the electrochemical method for electrode modification.

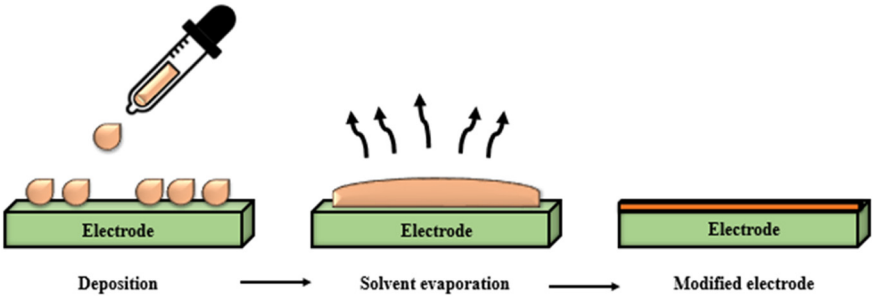

Fig. 3 Schematic diagram of the drop casting method for electrode modification.

successful monitoring of cell viability and screening the susceptibility of metabolically active cells to antibiotics, suggesting that the developed assay is suitable for cell proliferation and cytotoxicity testing.[74]

Finally, the method of spray coating (Fig. 4) is done with the help of a gravity feed airbrush under nitrogen pressure conditions on the center part of the electrode by masking the outer edges. For this coating technique, multiple applications are required to ensure a uniform distribution of the modifier.[29]

Jayabalan *et al.* (2020) used the spray coating method to modify nickel foam electrodes with a metal oxide/graphene nanocomposite to enhance hydrogen production from sugar industry wastewater in a microbial electrolysis cell. The results showed that the MEC performance for hydrogen production and COD removal was 2.68 and 1.15 times higher than that of an uncoated Ni foam electrode, respectively, therefore demonstrating the advantages in the use of modified electrodes for H_2 production and industrial effluent treatment in MECs.[75]

The spray coating method was also utilized by Sekar *et al.* (2019) to modify a carbon paper anode with Cu-doped iron oxide nanoparticles to enhance power generation and treatment of dairy wastewater in MFCs. The Cu-doped FeO-coated anode showed good hydrophilic property, increased potential (778 mV) and decreased resistance (0.190 Ω) when compared to the uncoated anode (670 mV and 12.09 Ω), and the performance of MFCs exhibited higher peak power density of 161.5 mW m^{-2} compared to 123.5 mW m^{-2} and COD removal efficiency 10% higher for the coated electrode, suggesting that the Cu-doped FeO nanoparticles can be an effective and cheaper material for treating dairy effluent and stimulating the energy production in MFCs.[76] Materials such as conductive polymers, carbon nanotubes, graphene, nitrogen and metal oxides have all been used as electrode modifiers with differing degrees of success.[37,77]

A great example of the success of the modifiers was demonstrated by Chaurasia and Mondal (2022), where the authors compared eight electrode combinations using the same substrate, reactor configuration and power supply. A nickel plate was used as the anode while eight different cathodes were developed through co-deposition of Ni, Ni–Co, and Ni–Co–P on the surface of SS316 and Cu rod by nickel electroplating techniques. The Ni–Co–P electrodeposited in both cases achieved the maximum HPR of 0.24 ± 0.005 m^3 m^{-3} d^{-1} and 0.21 ± 0.005 m^3 m^{-3} d^{-1} for SS316 and Cu, respectively, while the plain Cu cathode resulted in a rate 4 times lower (0.05 ± 0.002 m^3 m^{-3} d^{-1}). Moreover, the Ni–Co–P coating on SS316 presents approximately four times more electrocatalytic activity than the control cathode (bare SS316) and around two times more on Cu when compared to bare Cu. It was also found that the produced cathodes can treat real wastewater efficiently with considerably more energy recovery than previously reported literature.[25]

Also highlighting the importance of modifiers is the study by Gupta, Das and Ghangrekar (2020), where four MECs were operated, one with a plain carbon felt cathode, and three using Pd, Ni, and Ni–Pd as cathode modifiers for enhancing the yield of H_2O_2. Carbon felt was used as the anode for all the above. The highest yields of H_2O_2 were 233 ± 16 mg L^{-1}

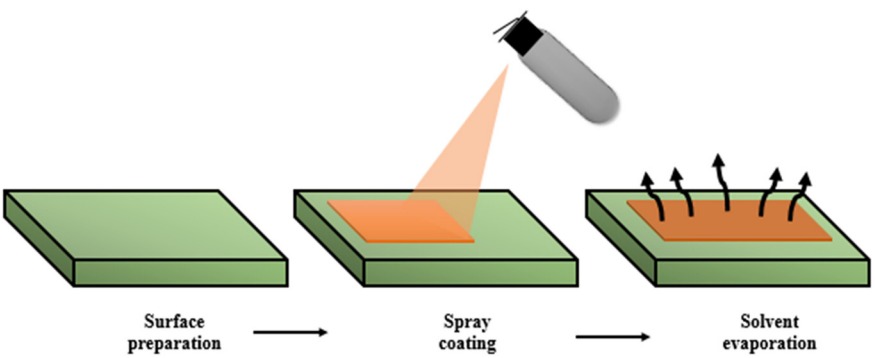

Fig. 4 Schematic diagram of the spray coating method for electrode modification.

d^{-1}, 197 ± 12 mg L^{-1} d^{-1} and 151 ± 11 mg L^{-1} d^{-1} for MEC-NiPd, MEC-Pd and MEC-Ni, respectively, being 3, 2.5 and 1.9 times more productive than the control MEC operated with a non-modified cathode. The same efficiency trend was also found in the COD tests, where MEC-NiPd displayed the best removal performance with 70 ± 3%, followed by MEC-Pd with 66 ± 3%, MEC-Ni with 57 ± 3% and finally, the control MEC with 43 ± 3% COD removal.[78]

Table 3 compiles studies that used nanocomposites as electrode modifiers in MECs for hydrogen and methane production and COD reduction. While nanomaterials are known in BES research for enhancing the attachment of bacteria on the electrode, most MEC studies have used nanocomposites as cathode modifiers while using carbon-based anodes.

4.2.1 Nanomaterials. The most used nanomaterials as electrode modifiers are metal–oxide nanocomposites and carbon nanotubes.[77] The biggest advantage of the first one is that metal–oxide nanocomposites can be prepared with several different porosities and structures that present high biocompatibility with host bacteria. Their disadvantage, however, is their low electrical conductivity, which can decrease the effectiveness of the BES. One of the possible solutions is for them to be used in composites along with other conductive materials.[79]

Carbon nanotubes (CNTs) are among the most promising electrode modifiers in bioelectrochemical systems. Their cylindrical nanostructure provides exceptionally high surface area (~1315 m^2 g^{-1}), high conductivity (100 MS m^{-1}), chemical inertness and mechanical stability, which generally results in an outstanding biocompatibility and microbial adhesion, and therefore, substantial enhancement in terms of power output and current production.[80,81] The main drawback of CNT-based anode modification is that it typically requires harsh chemical treatments (*e.g.*, HNO_3/H_2SO_4) and lengthy processing steps, which increase cost and complexity and may limit feasibility for large-scale applications.[77]

Table 3 compiles studies which used modified electrodes in their MECs. The table is divided into two parts, where the first one consists of purely metal-modified cathodes while the second section consists of cathodes modified using both metal and carbon-based materials.

In terms of hydrogen production, several modified electrode configurations have shown highly promising results, such as 223 ± 18 m^3 m^{-3} d^{-1} when using Cu/Ni as the cathode and graphene felt as the anode,[21] 81 ± 3.0 m^3 m^{-3} d^{-1} when using NiMo/graphene as the cathode and graphite block as the anode,[82] and 61.8 ± 2.0 m^3 m^{-3} d^{-1} for the Pd/carbon cloth cathode + carbon brush anode combination.[83] However, all these results were obtained using sodium acetate, which is considered a simple substrate. More studies should be carried out using these electrodes with more complex substrates to better characterize their efficiency.

Modified electrodes have also delivered strong results for wastewater treatment. High COD removal efficiencies were found using Cu/Ni, Pt/C cloth and Pt/Ti mesh as cathodes and graphene felt as anodes, with 76 ± 3%, ~80%, and 94 ± 0.5% removal, respectively.[21,62,84] Moreover, a 92% removal of antimony was reported by Dai *et al.* (2023) when using a ZIF67/carbon cloth cathode and a carbon cloth anode in synthetic wastewater.[85] NH_3 and PO_4^{3-} were also successfully removed (68.7% and 98.6%, respectively) from urine wastewater using a combination of MoS_2/nanocarbon cathode and carbon fiber brush anode.[26]

Overall, studies employing electrode modifiers are more comprehensive than those in section 4.1, as they typically compare at least two scenarios by altering a key parameter and evaluating its impact on MEC performance. Chaurasia and Mondal (2022) investigated several electrode material and modifier combinations with the same system configuration for treatment of sugar industry effluent and found a variation of 20.8 to 26.2 A m^{-2}, 0.17 to 0.24 m^3 m^{-3} d^{-1}, and 47% to 50% for CD, HPR and COD removal, respectively.[25] Moreover, Jwa *et al.* (2021) compared the efficiency of hydrogen production using a metal and a carbon electrode, both modified with platinum, and proved that although the CD obtained with the metal electrode was around six times superior, the hydrogen production remained basically the same due to the higher biocompatibility of the latter. Although measured, COD values were not reported in this work.[86]

The most comprehensive study identified in this review was conducted by Posadas-Hernández *et al.* (2023), which systematically evaluated cathode/anode pairings across carbon–carbon, metal–metal, metal–carbon, and modified metal–carbon configurations. Out of these, the ones with the most satisfactory HPR and COD removal were found for the SS cathode and anode and Cu-modified Ni cathode/SS pleated mesh anode with 314 ± 17 m^3 m^{-3} d^{-1} and 79 ± 4%, and 274 ±15 m^3 m^{-3} d^{-1} and 76 ± 3%, respectively, while the least satisfactory results were found for the combination of SS flat mesh anode and cathode and graphene felt cathode and anode, with 7.4 ± 1 m^3 m^{-3} d^{-1} and 6 ± 1%, and 1 ± 0.3 m^3 m^{-3} d^{-1} and 6 ± 1%, respectively.[21]

In conclusion, the majority of the articles used (87.5%) involves the modification of carbon-based electrodes, mainly cathodes, using metal-based nanocomposites, possibly to increase the conductivity (due to the use of metals) of the cheaper carbon materials. On the other hand, only 12.5% of the studies found used a combination of metals and carbon to modify the carbon-based cathodes.

4.2.2 Polymers. Conductive polymers, owing to their one-dimensional structures, have gained increasing attention as electrode modifiers in BES. They not only enhance bacterial adhesion and anodic performance but also interact directly with cell membranes, facilitating extracellular electron transfer.[79,97] Also, their ability to adsorb proteins and biomolecules from the culture medium promotes microbial growth and biofilm formation while simultaneously reducing interfacial resistance and increasing the availability of redox-active sites at the anode.[80,98]

Polyacrylonitrile (PAN) was used to modify a carbon felt electrode in a single-chamber MEC for ammonium oxidation

under different low C/N ratios (0, 1, and 1.5) and applied voltage of 0.6 V. The results were satisfactory and the dominant genera found on the electrodes were *Truepera*, *Aquamicrobium*, *Nitrosomonas*, *Arenimonas*, *Comamonas*, and *Cryobacterium.*[99]

Furthermore, in the study carried out by Park and collaborators (2023), poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) was used to modify a three-dimensional carbon felt anode to enhance the hydrogen production efficiency; PEDOT is known for its high conductivity and PSS presents super-hydrophilicity. As a result, the PEDOT:PSS-modified anode achieved twice as much hydrogen production when compared to the non-coated anode, since there was also 239.3% increase of capacitance current and 220.7% increase of biofilm formation. Additionally, the coated electrode decreased the time required for the MEC to reach a steady state of hydrogen production by 14 days and had a superior abundance of electrochemically active bacteria than the unchanged electrode. Moreover, although measured to calculate the CE of the system, COD removal was not reported in this work.[100]

Similarly, Spiess *et al.* (2021) modified carbon felt electrodes with poly(neutral red) and chitosan to be used in microbial electrolysis cells (MECs) for methane production at an applied potential of 400 mV. The most abundant microorganism species found in the biofilm created after a month of operation was *Enterococcus*. The results showed that both systems with the different modified electrodes achieved a HPR of 0.41 mmol L^{-1} d^{-1}, while the unmodified electrode achieved only 0.11 mmol L^{-1} d^{-1}. For COD removal efficiency the values obtained were 56%, 52% and 25% for chitosan-modified, poly(neutral red)-modified and unmodified electrodes, respectively.[101]

Because the use of polymer modifiers in MECs is still recent, the number of available studies is insufficient for a tabulated compilation or critical comparison. Nevertheless, the results reported so far highlight conductive polymers as highly promising electrode modifiers. Their one-dimensional electronic band structures enhance electron transfer and microbial adhesion, suggesting that this approach merits deeper investigation in future research aimed at improving hydrogen production and COD removal in MECs.

5. Identified research gaps

Although MEC research has expanded rapidly, several critical gaps limit translation to practice. Most studies remain confined to synthetic wastewaters or simple substrates such as acetate, which provide high hydrogen yields but fail to capture the complexity of real industrial, agricultural, or municipal effluents. These wastewaters contain inhibitory and unpredictable constituents that can suppress both organic matter removal and hydrogen purity. Equally, the effects of operational variables such as applied voltage, electrode spacing, hydraulic retention time, and organic loading are rarely optimized in a systematic way.[22,25,102]

Biological constraints also remain understudied. Hydrogen-consuming organisms, including methanogens and homoacetogens, often diminish hydrogen recovery, yet suppression strategies such as pH control or shortened retention times are inconsistently applied and seldom validated in long-term trials.[23,84,87] Similarly, few studies address energy efficiency comprehensively—balancing hydrogen recovery with minimal energy input and losses from overpotentials, membrane resistance, or side reactions—which complicates the scaling of MEC systems.[87]

Microbial community engineering represents another overlooked frontier. Although exoelectrogenic species underpin MEC function, there is limited research into enrichment or adaptation strategies to enhance electron transfer, stabilize biofilms, and increase tolerance to complex or inhibitory substrates. Without deliberate microbial optimization, electrode colonization and electron transfer efficiency remain vulnerable to fluctuations in feed conditions.[89]

Material durability is a further challenge. Non-noble metal cathodes such as Ni, SS, Co, and Mo are attractive for cost reasons, but they face corrosion, dissolution, and fouling in real wastewater environments. These processes undermine long-term catalytic activity, and while protective coatings and alloy optimization have been proposed, extended operational testing is rare.[1,87,93]

Finally, the absence of standardized methodologies limits progress. Differences in reactor design, substrate concentration, and analytical approaches prevent meaningful comparison across studies. Moreover, techno-economic analyses and life cycle assessments are scarce, leaving uncertainty about the real cost advantages and scalability of MECs for wastewater treatment and hydrogen generation.[1,25,87]

6. Future trends: polymer-nanocomposite modifiers and 3D electrodes

Some modifiers, such as the carbon nanotubes and nanocomposites, due to their unique structural and electrical properties, present good advantages for their use in BES. However, they are also considered toxic for the cells of some bacteria, which could cause an inhibition of proliferation and even cell death, decreasing the feasibility of their use. Therefore, some studies have been carried out aiming at the combination of these modifiers with nontoxic ones, such as polymers.[77] Currently, there are very few data of this technique being used for microbial electrolysis cell, but it has presented some satisfactory results in studies using microbial fuel cells.[98,103,104]

One research article using polymers in MECs was found in the search criteria used in the present review paper. In it, Ghasemi *et al.* (2020), produced a cathode electrode using polyaniline (PANI) and graphene on a stainless steel mesh (SSM) for hydrogen production using dairy wastewater as substrate and an applied potential of 1 V. They obtained a HPR

of 0.805 m^3 m^{-3} d^{-1}, while the COD removal reached 82%. These values were only 20% and 7% lower than those of the MEC with a Pt/carbon cloth cathode, while the fabrication cost of the modified cathode was 50% lower. Therefore, these results suggest that the PANI-graphene/SSM cathode is a satisfactory and cheaper alternative for hydrogen production using dairy wastewater as a substrate.[105]

Thus, it is believed that the next steps for the improvement of MECs are the implementation and study of polymer nanocomposites in these systems, aiming for better electrochemical activity, hydrogen production and COD and nutrient removal at a substantially lower cost.

Another modification on MECs that is expected to be approached more often in the future is the use of 3-dimensional electrodes in place of the regular flat ones. Similar to the polymer nanocomposite modifiers, this technique has been used more often in MFCs but is slowly spreading into MECs. A study carried out by Kadhim and Abbar (2023) used a rotating cylindrical porous graphite anode and a spiral-wound woven wire mesh rotating cylinder as the cathode for the removal of nickel from simulated wastewater. The best operating conditions were an applied voltage of 1.1 V, an initial nickel concentration of 100 ppm, an initial pH of 6, and a rotation speed of 300 rpm, achieving a nickel removal efficiency of 99.7% with an energy consumption of 0.88 kWh kg^{-1} Ni.[67]

Furthermore, some researchers choose to use carbon-based materials only for the anode of their system. Wang *et al.* (2019) produced a self-supported 3D porous carbon aerogel (CA) anode to be used in a MEC system for hydrogen production with an applied potential of 0.3 V and a platinum cathode. The results showed that the developed anode presented high specific surface area, excellent electrical conductivity and enhanced interaction with microbial communities, which therefore increased the bacterial incubation and favored the extracellular electron transfer. The authors then compared the HPR of CA/Pt with the one obtained using carbon fiber (CF) as the anode and observed that CA/Pt produced 5 times more hydrogen than CF/Pt with 0.37 μmol cm^{-2} h^{-1} and 0.007 μmol cm^{-2} h^{-1}, respectively.[63]

These few studies found indicate that the idea of using 3D electrodes in MECs can be very satisfactory for both wastewater treatment and hydrogen production, which brings up the possibility of more and more studies to investigate this configuration in microbial electrolysis cells in the near future.[106]

7. Conclusions

Electrodes remain the defining component of microbial electrolysis cells, dictating both efficiency and cost. Evidence across 41 studies shows that carbon-based anodes and metal cathodes, particularly stainless steel and nickel, consistently deliver the highest hydrogen yields and organic matter removal, with modified electrodes achieving COD reductions above 90% and hydrogen production rates exceeding 300 m^3 m^{-3} d^{-1}. Crucially, these performances approach platinum benchmarks at less than half the cost.

Yet, MEC research is still dominated by short-term tests with simple substrates, leaving key questions unanswered: how do these systems behave under the variability of industrial and municipal wastewaters? How durable are non-noble metals in corrosive environments? And what microbial strategies will ensure stable electron transfer at scale?

The most promising innovations, polymer nanocomposite modifiers and three-dimensional electrode architectures, offer a path forward by combining high conductivity, biocompatibility and surface area with affordability. To move from laboratory promise to real-world application, the field must move to long-term pilot testing, standardized performance metrics, and techno-economic analyses.

If these challenges are met, MECs could shift from experimental to a more attractive sustainable wastewater treatment option of producing clean water, recovering nutrients, and generating renewable hydrogen in a single, integrated process.

Conflicts of interest

The authors declare no conflict of interest.

List of abbreviations

BES	Bioelectrochemical system
CD	Current density
CE	Coulombic efficiency
COD	Chemical oxygen demand
EET	Extracellular electron transfer
GHG	Greenhouse gas
HER	Hydrogen evolution reaction
HPR	Hydrogen production rate
MDC	Microbial desalination cell
MEC	Microbial electrolysis cell
MES	Microbial electrosynthesis
MFC	Microbial fuel cell
PEM	Proton exchange membrane
SS	Stainless steel
WWTP	Wastewater treatment plant

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary information (SI). Raw data that support the findings of this study are available from the corresponding author upon reasonable request. Supplementary information is available. See DOI: https://doi.org/10.1039/d5ew00848d.

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