



REVIEW ARTICLE

Conductive Polymers in Microbial Fuel Cells for Bioelectricity Generation

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Received: 20 August 2026, Revised: 22 September 2026, Accepted: 23 September 2026, Published: 03 October 2026

Abstract

Microbial fuel cells (MFCs) offer simultaneous wastewater treatment and electricity generation, but their practical performance is limited by inefficient extracellular electron transfer (EET) and interfacial losses at the electrode–biofilm interface. Conductive polymers (CPs), particularly polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT), have therefore been investigated as electrode modifiers because their electrical, electrochemical, and surface properties can be tailored to support biofilm development and electron transfer. This review critically evaluates reported evidence for CP-modified MFC electrodes, with emphasis on electrochemical performance, EET-related mechanisms, microbial interactions, real-wastewater applications, stability, and scale-up limitations. Laboratory studies demonstrate substantial performance improvements under controlled conditions. For example, PANI nanofiber-modified carbon cloth reached a maximum power density of $1,091 \text{ mW m}^{-2}$, PPy/MXene-modified graphite felt reached 264 mW m^{-2} (vs. 45 mW m^{-2} for bare graphite felt), and a PEDOT-modified graphite-felt system treating palm oil mill effluent reported a maximum current density of 3.5 A m^{-2} and a Coulombic efficiency of 51%. However, these results are difficult to compare directly because studies differ in electrode architecture, reactor configuration, substrate, inoculum, and performance normalization. Evidence for specific CP-mediated EET mechanisms also remains limited, particularly for distinguishing direct, mediated, and long-distance electron-transfer contributions. More importantly, long-term operation with real wastewater and pilot-scale CP-modified systems remains insufficiently investigated. Existing pilot-scale MFC studies without CP modification demonstrate that performance under real wastewater conditions can differ substantially from laboratory results. Future research should therefore prioritize standardized performance reporting, matched real-wastewater comparisons, long-term stability testing, pilot-scale validation, mechanistic EET characterization, and fabrication-cost assessment. Overall, CPs show considerable potential for improving MFC electrode performance, but their practical and economic advantages over conventional electrodes remain to be established under realistic operating conditions.

Keywords: Conductive polymers, extracellular electron transfer, microbial fuel cells, polyaniline, polypyrrole

Introduction

Microbial fuel cells (MFCs) are bioelectrochemical systems that can simultaneously treat organic wastewater and recover electrical energy. It is a bioelectrochemical device in which

electroactive microorganisms oxidize organic substrates under anaerobic conditions, coupling that metabolism to reduction of an external electron acceptor through an external circuit and thereby generating electrical current [1], [2]. The theoretical open-circuit voltage (OCV) available from acetate oxidation (-0.296 V vs. standard hydrogen electrode (SHE)) coupled to oxygen reduction ($+0.816$ V vs. SHE) is approximately 1.1 V [2], yet practical operating voltages under load are typically 0.3 – 0.6 V, with the deficit attributable to activation, ohmic, and concentration overpotentials at both electrodes. Anode activation losses associated with extracellular electron transfer (EET) can represent an important limitation in MFC performance and are therefore a major target for electrode modification [3], [4].

Several reviews have surveyed electrode modification strategies for MFC anodes and have included conductive polymers (CPs) among other modification approaches [4]–[6]. The present review differs in three respects. First, it evaluates each CP individually rather than treating all CP modifications as equivalent, and explicitly separates polymer-specific contributions from those attributable to composite components, electrode morphology, and substrate architecture. Second, it applies an evidence-quality framework to distinguish directly demonstrated effects from correlative observations and materials-level inferences. Third, it systematically compares CP-modified laboratory results against pilot-scale benchmarks from non-CP MFC systems, providing a realistic assessment of the gap between what has been demonstrated under controlled conditions and what is known about practical performance. The key analytical conclusion this framework supports is that conductive polymers can measurably improve MFC electrode performance under laboratory conditions, but polymer-specific mechanistic superiority, long-term durability, and practical economic advantage over conventional electrodes remain to be established under realistic operating conditions.

Conventional carbon materials such as carbon felt (CF), carbon cloth (CC), and graphite felt (GF) provide electrically conductive and biocompatible electrode surfaces, but their surface chemistry and architecture may limit microbial attachment and interfacial electron transfer [7], [8]. Charge transfer resistances measured by electrochemical impedance spectroscopy (EIS) on bare GF consistently reach several ohms, representing the kinetic barrier that limits current. CPs may improve electrode performance through changes in surface area, electrical conductivity, surface charge, electrochemical activity, and biofilm electrode interactions [9]. Despite this mechanistic rationale and a large volume of published laboratory results, a gap exists between what has been demonstrated under idealized conditions and what can be achieved at operationally relevant scales with real wastewater over meaningful timescales. Accordingly, this review critically evaluates the reported performance of CP-modified MFC electrodes, with particular emphasis on mechanistic evidence, real-wastewater applications, stability, and scale-up limitations.

Literature search methodology

This is a critical narrative review rather than a systematic review: no formal Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) protocol was applied and no quantitative meta-analysis was performed. Literature was identified through searches of Web of Science, Scopus, and Google Scholar using terms including “microbial fuel cell” combined with “conductive polymer,” “polyaniline,” “polypyrrole,” “PEDOT,” “anode modification,” “extracellular electron transfer,” “wastewater treatment,” “pilot scale,” and “polymer stability.” The search covered primarily publications from 2005 to 2026. Studies were included if they reported quantitative electrochemical performance data for CP-modified MFC electrodes together with an unmodified control under comparable conditions, or if they provided mechanistic, stability, or real-wastewater data relevant to the review scope. Composite electrode studies were included to provide performance context but are distinguished from polymer-only modification studies throughout. Pilot-scale MFC studies without CP modification are included as contextual benchmarks. The exact number of papers screened is not reported because the

search was iterative rather than structured. All numerical values cited in this review are drawn from the original primary publication and were verified against that source.

MFC operating principles and the case for conductive polymers

A microbial fuel cell couples microbial oxidation of organic substrates at the anode with reduction of a terminal electron acceptor at the cathode. In a conventional dual-chamber configuration, the anode chamber is maintained under anaerobic conditions and contains the substrate and electroactive microorganisms, whereas the cathode chamber contains an electron acceptor such as dissolved oxygen or, in some laboratory systems, ferricyanide. Electrons released during microbial substrate oxidation are transferred to the anode through extracellular electron-transfer pathways and subsequently flow through an external circuit to the cathode, where they participate in the reduction reaction. Protons and other charge-balancing ions are transported through the separator or membrane between the two chambers. The overall cell voltage is lower than the theoretical value because of kinetic polarization at the electrodes, ohmic resistance in the electrodes, electrolyte and separator, and concentration or mass-transfer limitations. Consequently, anode modification is commonly investigated as one approach for improving electron-transfer kinetics and reducing anodic polarization [2], [10], [12].

Conductive polymers occupy an important position within the broader landscape of MFC anode-modification strategies, alongside metal and metal-oxide modifiers, carbon nanomaterials such as carbon nanotubes (CNTs), graphene and related derivatives, heteroatom-doped carbons, and biological or biointerface-oriented surface treatments [5], [6]. Common CPs investigated for MFC electrodes include polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT). Their appeal arises from the combination of electronic conductivity, electrochemical activity, tunable surface chemistry, and compatibility with composite architectures [5], [6]. Unlike carbon nanomaterials that primarily contribute high electrical conductivity and electroactive surface area, CPs can additionally provide chemically tunable interfaces through their conjugated backbones, doping/dedoping behavior, and functional groups, which can influence charge-transfer processes and microbial attachment at the electrode–biofilm interface [6]. Experimental studies have demonstrated that PANI- and PPy-based coatings and composites can improve MFC performance, while incorporation of carbon nanomaterials can further enhance the electrochemical properties of CP-based anodes through synergistic effects [5], [13]. The central issue is therefore not whether CPs can enhance MFC performance under laboratory conditions, but whether their electrochemical benefits can be translated into stable, reproducible, cost-effective, and practically deployable anodes. Important considerations include polymer loading, long-term coating stability, possible polymer detachment, mass-transfer effects, biofilm compatibility, synthesis complexity, material cost, and performance under real wastewater conditions [6].

Table 1. Electrochemical performance of bare carbon, CP-modified, and composite CP-modified MFC anodes

Anode system	Substrate & scale	Maximum power density	OCV / voltage	Citations
Bare graphite felt (GF)	Synthetic acetate; lab	45 mW m ⁻²	101 mV	[14]
MXene@GF	Synthetic acetate; lab	197 mW m ⁻²	157 mV	[14]
PPy/MXene@GF	Synthetic acetate; lab	264 mW m ⁻²	281 mV	[9]
PANI-modified carbon cloth	Synthetic acetate; 14 mL	777 mW m ⁻²	N/R	[9]
PANInf@carbon cloth (~50 nm fibers)	Synthetic acetate; 14 mL	1,091 mW m ⁻²	N/R	[9]
PEDOT@GF (2.5 mg cm ⁻² optimum)	POME wastewater; lab	3.5 A m ⁻² maximum current density; CE: 51%	N/R	[15]

Anode system	Substrate & scale	Maximum power density	OCV / voltage	Citations
SS/PANI-W	Synthetic; air-cathode MFC	$0.288 \pm 0.036 \text{ mW cm}^{-2}$	N/R	[16]
SS/PPy-W	Synthetic; air-cathode MFC	$0.187 \pm 0.017 \text{ mW cm}^{-2}$	N/R	[16]
Bare SS-W (control)	Synthetic; air-cathode MFC	$0.127 \pm 0.011 \text{ mW cm}^{-2}$	N/R	[16]
PPy@GF	Synthetic; dual-chamber MFC	919 mW m^{-2}	N/R	[17]
S-MXene/PPy hydrogel@CF	Synthetic; lab	8.05 W m^{-3}	646 mV	[18]
MXene/PPy@CF	Synthetic; lab	6.03 W m^{-3}	623 mV	[18]
PPy-only@CF	Synthetic; lab	4.91 W m^{-3}	594 mV	[18]
Bare CF (control)	Synthetic; lab	4.05 W m^{-3}	574 mV	[18]
PANI@nickel foam (NF)	Real leather tannery wastewater; dual-chamber lab MFC	373.01 mW m^{-2}	N/R	[19]
PANI@carbon felt (CF)	Real leather tannery wastewater; dual-chamber lab MFC	234.67 mW m^{-2}	N/R	[19]

N/R = not reported in the cited source. Values are reported using the units given in the original publications. Power-density values reported as W m^{-3} , mW m^{-2} , and mW cm^{-2} are retained in their original forms and should not be considered directly comparable because reactor configuration, electrode geometry, normalization basis, and operating conditions differ among studies. GF = graphite felt; CF = carbon felt; CC = carbon cloth; NF = nickel foam; S-MXene = sulfur-doped MXene; SS-W = stainless-steel wool; PANInf = polyaniline nanofiber; POME = palm oil mill effluent; PANI = polyaniline; PPy = polypyrrole; PEDOT = poly(3,4-ethylenedioxythiophene); CE = Coulombic efficiency; Rct = charge-transfer resistance; COD = chemical oxygen demand.

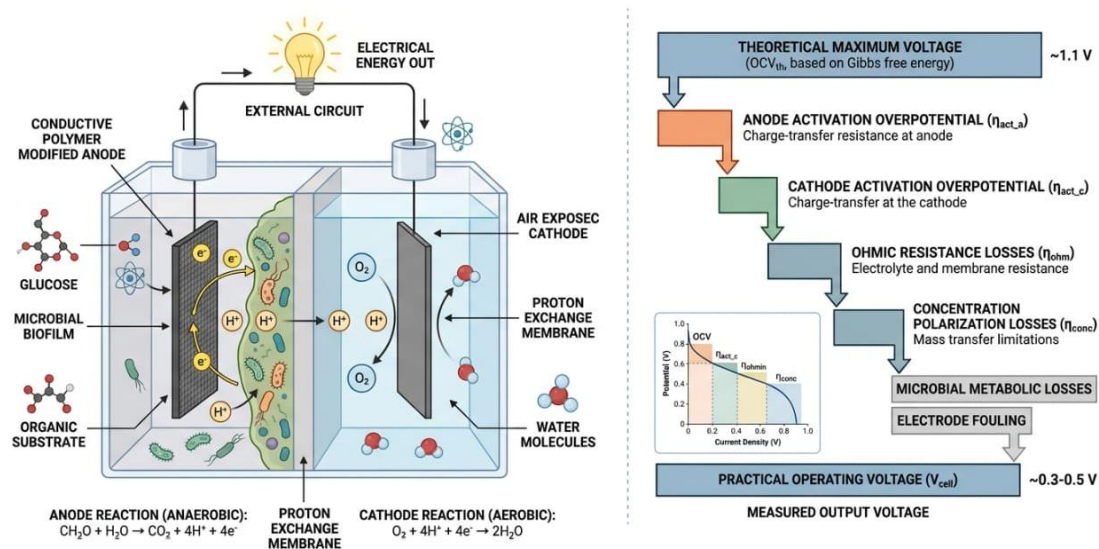


Figure 1. Dual-chamber MFC operating principles.

Left: anaerobic anode chamber with CP-modified electrode (orange) supporting electroactive biofilm; proton exchange membrane (PEM); aerobic cathode; external circuit with load. Right: voltage loss cascade from theoretical OCV ($\sim 1.1 \text{ V}$ for acetate/ O_2 [2]) to practical operating voltage, with anode activation overpotential identified as the primary CP modification target. Original schematic from Rabaey & Verstraete [2] thermodynamic values; diagram is an original synthesis for this review.

Extracellular electron transfer and the CP electrode interface

Three major EET mechanisms are commonly discussed at MFC anodes: direct electron transfer (DET), mediated electron transfer (MET), and long-distance extracellular electron transfer (LDET). Direct electron transfer (DET) involves electron transfer through cell-surface redox proteins, including OmcE, OmcS, and OmcZ in *Geobacter sulfurreducens* and OmcA and MtrC in *Shewanella oneidensis* MR-1 [20]. DET generally requires close interaction between microorganisms and the extracellular electron acceptor; however, current generation in electroactive biofilms is not necessarily restricted to a single cell layer directly contacting the electrode because extracellular conductive structures can facilitate electron transfer from cells located deeper within the biofilm. Mediated electron transfer (MET) involves soluble or diffusible redox-active compounds that shuttle electrons between microorganisms and the electrode. In *S. oneidensis* MR-1, secreted flavins, including riboflavin and flavin mononucleotide (FMN), contribute to extracellular electron transfer [21]. LDET through electrically conductive pili was demonstrated in *Geobacter* by Reguera et al. [22]: a pili-deficient mutant attached to Fe(III) oxides but could not reduce them, while conducting-probe atomic force microscopy (AFM) independently confirmed pili conductivity [22]. LDET can enable microorganisms located within deeper regions of electroactive biofilms to contribute to extracellular electron conduction, allowing thicker biofilms to remain electrochemically active beyond the immediate electrode interface [23], [24], which is why three-dimensional CP architectures that accommodate deep biofilm penetration are mechanistically well-motivated, as demonstrated for 3D carbon nanotube scaffolds [25].

CP coatings can potentially influence several EET-related processes by modifying the physicochemical properties of the electrode–biofilm interface. For DET, increased effective surface area, particularly in PANI nanofiber networks with approximately 50 nm fiber diameter, can provide additional sites for bacterial attachment and electrode interaction [9]. The positively charged PANI surface at near-neutral pH promotes bacterial attachment through electrostatic interactions with negatively charged bacterial cell surfaces (typical Gram-negative zeta potential: -10 to -30 mV), although direct zeta potential measurements under MFC conditions remain limited. For MET, the electrochemical activity of CPs provides a potential mechanism for interaction with extracellular redox-active compounds; however, direct evidence that PANI or PPy functions as a specific flavin-redox relay in MFC anodes remains limited. Therefore, the proposed contribution of CPs to flavin-mediated electron transfer should currently be regarded as a mechanistic possibility rather than an experimentally established mechanism. For LDET, three-dimensional CP hydrogel and nanofiber architectures may increase the accessible electrode surface and support biofilm development throughout the electrode structure. However, direct evidence that CP architectures specifically enhance long-range electron transfer through microbial conductive structures remains limited. Bi et al. [18] reported a 45.34% relative abundance of *Geobacter* on the S-MXene/PPy anode based on 16S rRNA sequencing, together with improved MFC performance. However, 16S rRNA sequencing identifies microbial community composition and does not by itself establish the specific EET mechanism responsible for the observed performance. Furthermore, no study identified in this review has applied a flavin-removal and reintroduction experiment analogous to Marsili et al. [21] to directly compare MET contributions between CP-modified and bare carbon anodes. Therefore, enhancement of flavin-mediated electron transfer by CPs remains mechanistically plausible but has not been directly quantified.

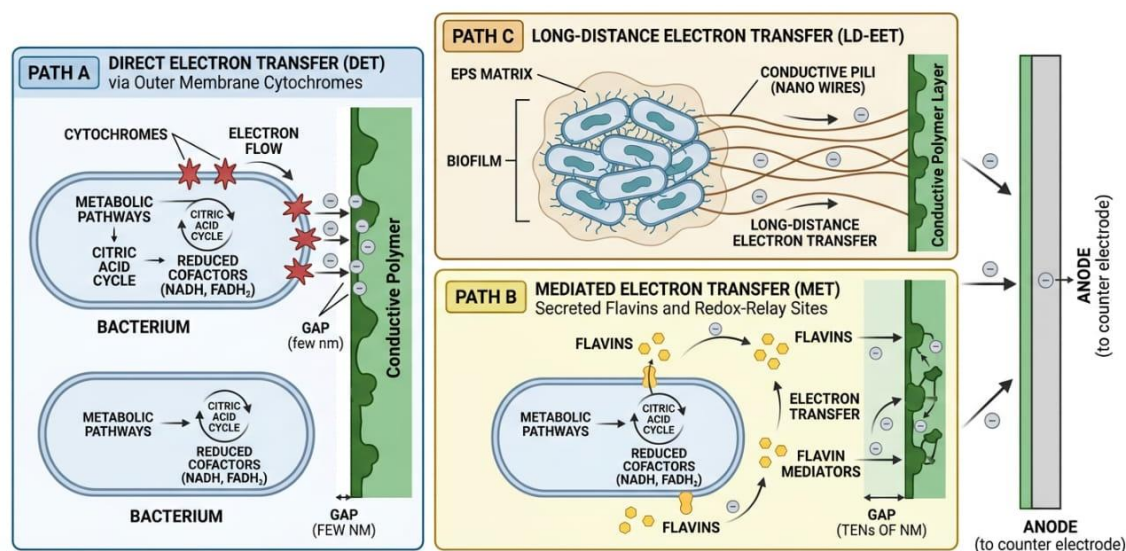


Figure 2. Three EET pathways at a CP-modified MFC anode.

Schematic of three established EET pathways (general MFC literature) at a CP-modified anode. Path A (DET): *Geobacter*-type cell transfers electrons via outer-membrane cytochromes (OmcZ/OmcS) to the anode surface; proposed extension to CP nanofibers is mechanistically plausible but not directly demonstrated on CP-modified electrodes. Path B (MET): *Shewanella*-type cell secretes riboflavin/FMN, which shuttles electrons to the electrode; a 70% current drop on flavin removal and 94% restoration on reintroduction [21] establish the MET pathway quantitatively for bare electrodes; whether CPs specifically enhance flavin-mediated MET has not been directly demonstrated. Path C (LDET): cells deeper in the biofilm transfer electrons via conductive pili; pili-deficient *Geobacter* mutant could not reduce Fe(III) despite attachment [22].

Critical evaluation of conductive polymers as MFC electrode modifiers Polyaniline (PANI)

Polyaniline is one of the conductive polymers investigated as an anode modifier in MFCs. Its electrical properties depend strongly on its oxidation state and protonation level. The protonated emeraldine salt form is substantially more conductive than the deprotonated emeraldine base, and reported conductivity values for PANI can range from approximately $\leq 10^{-10} \text{ S cm}^{-1}$ for undoped emeraldine base to $\geq 10 \text{ S cm}^{-1}$ for doped emeraldine salt, although these values depend strongly on the dopant, morphology, processing conditions, and measurement conditions [26]. Importantly, conductivity values obtained under conventional polymer-characterization conditions should not be interpreted directly as the conductivity of PANI during MFC operation.

Morphological engineering can improve the electrochemical performance of PANI-modified anodes. Ahmed and Kim [9] compared a PANI nanofiber-based anode (PANInf) with a PANI-modified anode and reported maximum power densities of 1,091 and 777 mW m^{-2} , respectively. The PANInf electrode also exhibited lower charge-transfer resistance and a higher current density, while microscopic observations indicated enhanced bacterial colonization of the nanofiber-modified electrode. These findings suggest that increasing the accessible three-dimensional electrode surface can improve microbial attachment and facilitate electron-transfer processes at PANI-modified anodes. However, the improvement should be attributed to the combined effects of electrode morphology, accessible surface area, bacterial colonization, and electrochemical properties rather than to PANI conductivity alone [9].

Earlier studies also demonstrate the potential of PANI-based anode modification. Lai et al. [27] reported a maximum power density of 5.16 W m^{-3} for a PANI-modified CC anode, corresponding to approximately 2.66-fold higher power density than that of the unmodified control. The study also reported lower internal resistance and a shorter start-up time for the

PANI-modified MFC, supporting an improvement in anode electrochemical performance. In another study, Sonawane et al. [16] investigated PANI-coated stainless-steel wool and reported higher power density than that obtained with bare stainless-steel wool and PPy-coated stainless-steel wool, demonstrating the potential of PANI modification for porous metallic anode structures.

Nevertheless, PANI performance is strongly dependent on its protonation state and the physicochemical conditions of the MFC. Because protonation contributes to the high conductivity of the emeraldine salt form, changes in pH and local electrochemical conditions can alter the electrical properties of PANI. Therefore, conductivity values obtained under strongly acidic polymer-characterization conditions should be interpreted cautiously when discussing PANI performance in the near-neutral conditions commonly used in microbial anodes. Direct measurements of PANI conductivity under actual MFC operating conditions remain limited, making it difficult to quantitatively separate the contribution of PANI conductivity from other factors such as electrode morphology, biofilm development, substrate composition, and electrode–biofilm interactions.

Evidence from real wastewater systems further illustrates the dependence of PANI-modified anodes on operating conditions. Mumtaz et al. [19] reported maximum power densities of approximately 373 mW m⁻² for PANI-modified nickel foam and 235 mW m⁻² for PANI-modified CF when treating real leather-tannery wastewater with a mixed microbial community. These results demonstrate that PANI-modified anodes can function with complex wastewater substrates, but the reported values should not be directly compared with values obtained using synthetic acetate because substrate composition, inoculum, electrode architecture, reactor configuration, and operating conditions differed among the studies. Consequently, differences in power density cannot be attributed solely to changes in PANI protonation or conductivity [19].

A further consideration is the long-term stability of PANI coatings. Repeated changes in the oxidation and protonation states of conducting polymers can induce structural and volumetric changes in polymer films, potentially affecting their mechanical integrity and adhesion to the underlying electrode. However, long-duration MFC studies specifically quantifying changes in PANI adhesion, conductivity, and electrochemical performance during extended operation remain limited. Thus, although PANI provides a potentially useful route for improving anode electrochemical performance, future studies should place greater emphasis on in situ characterization of conductivity, coating stability, adhesion, biofilm development, and long-term performance under realistic wastewater conditions. Electrode wettability is an additional parameter warranting systematic investigation: contact angle measurements show that CP modification can substantially alter the hydrophilicity of carbon anodes, with lower contact angles generally associated with improved electrolyte penetration and biofilm adhesion [12]. Comparative wettability data for PANI-, PPy-, and PEDOT-modified anodes under standardized conditions remain scarce, and future studies are encouraged to include contact angle measurements alongside electrochemical characterization.

Polypyrrole (PPy)

Polypyrrole is another widely investigated conductive polymer for MFC anode modification. Compared with PANI, PPy can retain electrical conductivity over a broader pH range because its conducting state is associated primarily with oxidation and charge compensation by counterions rather than the acid–base protonation/deprotonation process that strongly controls the conductivity of PANI. Experimental studies have shown that PPy can retain measurable conductivity under neutral and even alkaline conditions, although its conductivity and electrochemical stability still depend on the polymer structure, dopant, morphology, and surrounding electrolyte [28].

Pu et al. [17] demonstrated the effectiveness of in situ PPy deposition on GF for improving MFC start-up performance. The PPy-modified anode reached a reproducible voltage platform in approximately 5 days, compared with 11 days for the unmodified GF anode, and achieved a

maximum power density of 919 mW m^{-2} , approximately 2.3-fold higher than the unmodified electrode. Microscopic and electrochemical analyses indicated that PPy increased electrode surface roughness and electrical conductivity and promoted faster microbial attachment and growth. These findings support a role for PPy modification in improving the electrode–microbe interface and accelerating MFC start-up, although the improvement cannot be attributed to bacterial adhesion alone.

Composite PPy systems have also produced substantial improvements in MFC performance. Batool et al. [14] compared bare GF, MXene-modified GF, and PPy/MXene-modified GF and reported maximum power densities of 45, 197, and 264 mW m^{-2} , respectively, with corresponding maximum output voltages of 101, 157, and 281 mV. The higher performance of PPy/MXene relative to the individual control electrodes indicates that combining PPy with MXene can modify the electrochemical properties of the anode; however, the experiment does not independently quantify the contribution of MXene surface area and PPy nitrogen-containing functionality.

Bi et al. [18] further evaluated PPy and PPy/MXene-based anodes using a four-condition design. The reported maximum power densities were 4.05 W m^{-3} for bare CF, 4.91 W m^{-3} for PPy-modified CF, 6.03 W m^{-3} for MXene/PPy-modified CF, and 8.05 W m^{-3} for S-MXene/PPy (sulfur-doped MXene/PPy)-modified CF. The corresponding maximum output voltages increased from 574 mV for the bare electrode to 646 mV for the S-MXene/PPy electrode. The study also used 16S rRNA sequencing to characterize the microbial community and reported a relative abundance of approximately 45.34% for *Geobacter* on the S-MXene/PPy anode. This result indicates enrichment of *Geobacter* under the tested conditions, but community abundance alone does not establish a specific EET mechanism or demonstrate that PPy directly caused the observed enrichment. The sulfur-doping strategy was introduced to modify the MXene structure and reduce nanosheet restacking, adding another material variable that should be considered when interpreting the performance improvement.

PPy has also been investigated in combination with carbon nanomaterials. Jung and Roh [29] developed carbon-nanofiber/PPy nanocomposite anodes and reported improved MFC power generation relative to the commercial GF control, while demonstrating the potential of PPy–carbon nanofiber architectures for improving electrode conductivity and electrochemical performance. Zou et al. [30] similarly reported a PPy-coated carbon-nanotube composite anode in a mediatorless MFC using *Escherichia coli*. At a PPy–CNT loading of 5 mg cm^{-2} , the electrode produced a maximum power density of 228 mW m^{-2} and outperformed the plain carbon-paper control.

Poly(3,4-ethylenedioxythiophene) (PEDOT)

PEDOT has attracted interest as an MFC electrode modifier because of its high electrical conductivity, electrochemical activity, and relatively favorable stability compared with several other conducting polymers. Its low electronic band gap facilitates charge transport and reversible electrochemical doping and dedoping. PEDOT:PSS formulations can achieve electrical conductivities approaching or exceeding 1000 S cm^{-1} following appropriate secondary treatments, although these values depend strongly on formulation, processing conditions, and post-treatment and should not be interpreted as the conductivity of PEDOT under MFC operating conditions.

Kang et al. [15] investigated different PEDOT loading levels on GF anodes and identified 2.5 mg cm^{-2} as the optimum loading under their experimental conditions. At this loading, the modified anode achieved a maximum current density of 3.5 A m^{-2} and a Coulombic efficiency (CE) of 51%. The study also reported enhanced selection of exoelectrogenic microorganisms on the PEDOT-modified biofilm and a reduction in the internal resistance of the MFC after anode modification. These results demonstrate that PEDOT loading and electrode architecture can substantially influence MFC performance. However, the reported performance should be interpreted as the combined effect of PEDOT coating, loading level, GF structure, and biofilm development rather than as evidence that PEDOT conductivity alone determines MFC output.

Earlier work by Kang et al. [31] similarly demonstrated a synergistic effect between PEDOT coating and the structural characteristics of the underlying anode. PEDOT was applied to graphite plate, CC, and GF, and the GF/PEDOT electrode achieved a maximum current density of 3.5 A m^{-2} , together with a Coulombic efficiency of 51% and chemical oxygen demand (COD) removal of 86%. The authors attributed the superior performance of GF partly to its open structure and high surface area, which provided a favorable electrochemical and microbial-growth environment. These findings reinforce the importance of separating the contribution of PEDOT from that of the underlying electrode architecture when comparing PEDOT-modified MFC anodes.

Evidence from defined microbial systems also provides mechanistic support for PEDOT-mediated improvement of the electrode–microbe interface. X. Liu et al. [32] investigated an electrochemically deposited PEDOT layer at the interface between *Shewanella loihica* and an anode. The PEDOT coating produced a nanoscale porous structure, increased the availability of redox-active sites, and reduced interfacial electron-transfer resistance. Compared with the unmodified electrode, the PEDOT-modified anode increased power density by approximately 43% to 140 mW m^{-2} . The authors proposed that direct electron transfer dominated at the PEDOT *S. loihica* interface. Importantly, the study also found that the porous PEDOT layer did not increase bacterial affinity or mediator affinity, indicating that its beneficial effect should not simply be interpreted as enhanced bacterial adhesion.

PEDOT:PSS, the most widely studied PEDOT formulation in the broader bioelectronics and energy literature, merits specific attention. In PEDOT:PSS, polystyrenesulfonate (PSS) serves as the counterion dopant and dispersant, enabling aqueous processing and film casting onto a wide range of electrode substrates. Secondary treatments such as ethylene glycol, dimethyl sulfoxide (DMSO), or concentrated sulfuric acid can substantially increase the conductivity of PEDOT:PSS films, in some cases reaching values exceeding 1000 S cm^{-1} , primarily by selectively removing insulating PSS-rich domains from the film, as reviewed in the conducting-polymer literature [5]. However, the very high conductivity values reported for treated PEDOT:PSS films are measured under dry conditions and do not reflect the conductivity of the hydrated, electrolyte-exposed film during MFC operation. In the MFC context, PEDOT:PSS has the practical advantage of commercial availability as an aqueous dispersion (e.g., commercial PEDOT:PSS dispersions such as Clevios PH 1000; Heraeus), which simplifies electrode preparation compared with in situ polymerization of 3,4-ethylenedioxythiophene (EDOT) monomer. Composite PEDOT/MnO₂ anode modification has also been reported: P. Liu et al. [33] used vapor-phase polymerization to deposit PEDOT/MnO₂ on CF and reported a maximum power density of $1,534 \pm 13 \text{ mW m}^{-2}$ with a charge-transfer resistance reduced to approximately $3.6 \text{ }\Omega$, compared with values exceeding $20 \text{ }\Omega$ for the unmodified CF. This composite approach illustrates a strategy in which PEDOT provides the conductive matrix while MnO₂ contributes additional pseudocapacitive and electrocatalytic properties, a design principle that has shown promise for enhancing both power output and biofilm–electrode interaction.

PEDOT is nevertheless less extensively investigated in MFCs than PANI and PPy. One practical consideration is the cost of EDOT and the additional processing requirements associated with PEDOT synthesis and deposition. In addition, PEDOT does not contain nitrogen-rich functional groups analogous to those present in PANI or PPy, and therefore surface interactions with microorganisms may differ among the polymers. However, the available evidence does not support describing the absence of nitrogen-containing groups as an absolute limitation for bacterial colonization. The studies of Kang et al. [31] and X. Liu et al. [32] demonstrate that PEDOT-modified electrodes can support electroactive biofilms and effective electrode–microbe electron transfer through a combination of surface morphology, electrochemical properties, and interfacial charge-transfer characteristics.

An important limitation is the lack of systematic long-term comparisons among PANI, PPy, and PEDOT under identical MFC operating conditions. Although PEDOT is widely regarded as a relatively stable conducting polymer, most MFC studies have focused on short- or

medium-term performance metrics such as current density, power density, Coulombic efficiency, and charge-transfer resistance rather than directly measuring polymer degradation, conductivity retention, adhesion, or structural changes during prolonged operation. Therefore, the proposed stability advantage of PEDOT should currently be regarded as a material-level expectation rather than a quantitatively demonstrated advantage under long-term MFC conditions. Future studies should directly compare PANI, PPy, and PEDOT using identical electrode substrates, microbial inocula, substrates, loading levels, and operating conditions while simultaneously monitoring polymer integrity, conductivity, adhesion, biofilm development, and electrochemical performance.

Polymer stability: mechanisms of degradation

Long-term stability is among the most critical and least well-characterized properties of conductive-polymer anode coatings in MFCs. Three principal degradation mechanisms have been identified in the broader electrochemical polymer literature and are directly relevant to MFC operating conditions: (i) electrochemical dedoping, in which repeated redox cycling or sustained anodic polarization partially or fully removes counterions from the polymer backbone, reducing conductivity; (ii) mechanical delamination, in which swelling and shrinkage associated with doping state changes generate mechanical stress at the polymer–electrode interface, leading to coating detachment over extended operation; and (iii) oxidative over-oxidation, in which exposure to reactive oxygen species or highly positive anode potentials irreversibly degrades the conjugated backbone, particularly in PPy and PANI [6], [28].

PANI is particularly susceptible to conductivity loss at near-neutral pH because the emeraldine salt form, which is responsible for high conductivity, requires protonation to maintain its charge-transfer properties. In near-neutral MFC anolyte (typically pH 6.5–7.5), progressive deprotonation toward the less-conductive emeraldine base form can occur during sustained operation, reducing the electrochemical contribution of PANI over time. Experimental evidence specifically quantifying PANI conductivity retention, charge-transfer resistance evolution, and coating adhesion at monthly intervals during MFC operation remains limited. The available data therefore does not permit a definitive conclusion on whether PANI coatings maintain their electrochemical contribution over timescales relevant to practical wastewater treatment.

PPy retains measurable conductivity over a wider pH range than PANI because its primary conducting mechanism depends on oxidation state and counterion compensation rather than acid–base protonation [28]. However, PPy is susceptible to over-oxidation under strongly anodic conditions, and mechanical delamination from GF substrates has been reported as a practical concern during extended operation. PEDOT, with its low band gap and relatively high intrinsic conductivity, is generally regarded as the most environmentally stable of the three polymers reviewed here, with PEDOT:PSS formulations showing conductivity retention over extended periods under ambient conditions. However, systematic in-situ conductivity measurements of PEDOT during long-term MFC operation (i.e., beyond 60 days) under continuous real-wastewater flow remain absent from the published literature.

A key methodological gap is the absence of standardized protocols for measuring CP stability during MFC operation. Future stability studies should at minimum report: (a) electrochemical impedance spectroscopy at regular intervals to track charge-transfer resistance evolution; (b) gravimetric or scanning electron microscopy assessment of coating integrity at the end of operation; (c) ex-situ conductivity measurements on retrieved electrode sections; and (d) power-density and current-density trajectories plotted continuously rather than reported only at a single time point. Until such standardized long-term datasets are available, the stability advantage of any particular CP formulation should be treated as inferred from materials characterization rather than demonstrated under MFC operating conditions.

Table 2. Mechanistic comparison of PANI, PPy, and PEDOT as MFC anode modifiers: verified performance, doping mechanism, failure mode, and evidence quality

Parameter	PANI	PPy	PEDOT
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Parameter	PANI	PPy	PEDOT
Power/current performance	PANI: 777 mW m ⁻² ; PANInf: 1,091 mW m ⁻² [9]	PPy/GF: 919 mW m ⁻² [17]	PEDOT/GF: 3.5 A m ⁻² maximum current density; CE: 51% [15]
Higher composite result	PANInf/CC: 1,091 mW m ⁻² (highest in reviewed dataset); no PANI/nanocarbon composite result in reviewed literature [9]	PPy/CNT hydrogel: 1,898 ± 46 mW m ⁻² [34]	PEDOT/MnO ₂ /CF: 1,534 ± 13 mW m ⁻² [33]
EIS / charge-transfer evidence	R _{ct} ≈ 44 Ω (PANI); ≈35 Ω (PANInf)	PPy/CNT composite: internal resistance decreased from 48 to 30 Ω [34]	R _{ct} decreased after biofilm formation [15]
Microbial/biofilm evidence	Bacterial attachment/biofilm observed; no 16S community profile reported in [9]	Faster microorganism attachment/growth on PPy/GF than bare GF [17]	<i>Geobacter</i> identified as a prevailing exoelectrogen in the studied system [15]
Real wastewater tested	Leather tannery wastewater; PANI@NF: 373.01 mW m ⁻² [19]	Not included	Palm oil mill effluent (POME); 3.5 A m ⁻² maximum current density; CE: 51% [15]

Conductive polymers at the cathode

Research on conductive-polymer modification in MFCs has focused predominantly on the anode, whereas cathode modification has received comparatively less attention. In air-cathode single-chamber MFCs, oxygen reduction at the cathode can represent an important source of polarization and voltage loss, particularly because the oxygen reduction reaction (ORR) is kinetically sluggish and often requires an electrocatalyst. ORR can proceed via two competing pathways: the four-electron pathway ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$), which maximizes current recovery, and the two-electron pathway ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$), which generates hydrogen peroxide as a by-product and represents a less efficient use of oxygen. Selectivity toward the four-electron pathway is therefore an important criterion for evaluating CP-based cathode catalysts. Platinum provides high ORR activity and strongly favors the four-electron pathway, but its high cost has motivated the development of less expensive catalyst systems. Conductive polymers have therefore been investigated both as electrode materials and, more commonly, as conductive supports or components of composite ORR catalysts. However, their catalytic contribution depends strongly on polymer type, oxidation state, dopant, morphology, and the incorporation of additional catalytic species.

Feng et al. [35] demonstrated the feasibility of a conductive-polymer-based MFC cathode by electropolymerizing a polypyrrole/anthraquinone-2-sulfonate (PPy/AQS) film directly onto stainless-steel mesh. The resulting cathode catalyzed oxygen reduction and enabled a membraneless MFC to generate electricity for more than 250 h, with a maximum power density of 575 mW m⁻². Increasing the PPy/AQS film thickness reduced performance, which was attributed to increased ohmic resistance and restricted oxygen diffusion within the cathode layer.

Yuan et al. [36] further demonstrated the potential of PANI as a conductive support for non-precious ORR catalysts. Their PANI/carbon-black-supported iron phthalocyanine (PANI/C/FePc) cathode showed enhanced ORR activity compared with carbon-supported FePc and produced a maximum power density of 630.5 mW m⁻² in an air-cathode MFC, compared with 336.6 mW m⁻² for the C/FePc cathode and 575.6 mW m⁻² for the Pt cathode under the conditions tested. The study therefore illustrates an important design strategy in which the

conductive polymer functions primarily as a conductive and catalyst-dispersing matrix, while the incorporated metal complex provides the principal ORR catalytic sites.

A brief performance comparison of the CP-based cathode systems discussed here is informative. The PPy/AQS cathode of Feng et al. [35] produced a maximum power density of 575 mW m^{-2} and sustained operation for more than 250 h in a membraneless single-chamber MFC; this represents a practically relevant duration for an initial feasibility demonstration. The PANI/C/FePc cathode of Yuan et al. [36] achieved 630.5 mW m^{-2} , modestly exceeding both the PPy/AQS result and the platinum-cathode control (575.6 mW m^{-2}) under the conditions of that study, which is noteworthy given the substantially lower cost of FePc relative to Pt. In both cases, however, the cathode performance should be evaluated in the context of the full MFC configuration, including separator type, anode material, reactor geometry, and electrolyte composition, all of which differ between the studies and preclude direct cross-study performance comparison. Furthermore, neither study reported the ORR pathway selectivity (two-electron versus four-electron) of the respective CP-based catalyst under MFC operating conditions, which is an important gap given that the two-electron pathway produces hydrogen peroxide as a by-product that can inhibit biofilm activity in single-chamber MFCs lacking a separator. Future cathode studies should therefore report ORR pathway selectivity, onset potential, long-term catalyst stability including catalyst leaching, and performance under standardized air-cathode conditions alongside power density and Coulombic efficiency.

Taken together, the available evidence indicates that the most promising role of conductive polymers at MFC cathodes is not necessarily as stand-alone ORR catalysts, but as conductive matrices, catalyst-supporting phases, or components of hybrid structures containing metal complexes, metal oxides, carbon materials, or other catalytic species. A major research need is therefore to distinguish the contribution of the polymer itself from that of the incorporated catalyst and carbon support. Future studies should report ORR pathway, charge-transfer resistance, oxygen-diffusion characteristics, polymer retention, catalyst leaching, and performance under prolonged operation using standardized cathode conditions. Systematic long-term comparisons of PANI-, PPy-, and PEDOT-based cathodes under realistic air-cathode MFC conditions specifically addressing ORR pathway selectivity, catalyst leaching, polymer retention, and performance stability over months of operation remain absent from the published literature.

Wastewater treatment

The most important interpretive problem in the conductive-polymer MFC wastewater-treatment literature is attributing improvements in COD removal to the electrode material when inoculum composition, substrate characteristics, reactor configuration, and operating conditions differ between compared systems. Stronger attribution requires matched experimental conditions, particularly when comparing modified and unmodified electrodes. Batool et al. [14], for example, used the same inoculum and substrate across the compared electrode conditions, whereas Kang et al. [15] demonstrated PEDOT-anode operation using both synthetic medium and palm oil mill effluent (POME). In a separate study, Mumtaz et al. [19] evaluated PANI-modified electrodes with a mixed microbial culture treating real leather-tannery wastewater and reported maximum power densities of 373.01 mW m^{-2} for PANI@NF and 234.67 mW m^{-2} for PANI@CF. However, differences in nutrient supplementation and catholyte conditions mean that the reported treatment and power performance should not be attributed exclusively to PANI. Kang et al. [15] demonstrated that a PEDOT-modified GF anode could operate with high-organic-loading POME wastewater, achieving a maximum current density of 3.5 A m^{-2} and a Coulombic efficiency of 51% at the optimum PEDOT loading of 2.5 mg cm^{-2} .

The pilot-scale literature provides an important benchmark for evaluating these laboratory-scale CP-MFC results. Rossi et al. [37] operated an 850-L air-cathode MFC treating real domestic wastewater for more than six months. The system produced an average power of $0.46 \pm 0.35 \text{ W}$, corresponding to 0.043 W m^{-2} based on projected anode area, with a hydraulic retention time (HRT) of 12 h and a Coulombic efficiency of approximately 9%. COD removal

in the MFC alone averaged $49 \pm 15\%$, whereas coupling the MFC with a downstream biofilter increased overall COD removal to $91 \pm 6\%$.

Other large-scale studies similarly demonstrate that substantial wastewater treatment can be achieved without conductive-polymer modification. Liang et al. [38] operated a 1000-L modularized MFC system for more than one year treating real municipal wastewater. COD removal remained in the range of 70–90%, while power density during municipal-wastewater treatment was $7\text{--}60 \text{ W m}^{-3}$. Das et al. [39] subsequently demonstrated a 720-L stacked MFC for on-site sanitary wastewater treatment, reporting approximately 87% COD removal under the reported operating conditions and a maximum power output of 61 mW. Large-scale studies such as these provide important context for interpreting CP-MFC claims because they demonstrate that substantial COD removal can be achieved through reactor configuration, hydraulic retention, microbial activity, and conventional electrode operation even in the absence of conductive-polymer modification.

The low Coulombic efficiency observed by Rossi et al. [37] (approximately 9%) also illustrates an important distinction between wastewater treatment and electricity recovery. COD removal represents a reduction in the measured chemical oxygen demand of the wastewater, whereas Coulombic efficiency reflects the fraction of substrate-derived electrons theoretically recovered as electrical current. Consequently, high COD removal does not necessarily indicate efficient electron recovery by the anode. In real wastewater, organic substrates can be consumed through competing biological pathways, including fermentation, methanogenesis, sulfate reduction, and biomass synthesis, in addition to anodic respiration. Therefore, improving electrode conductivity or extracellular electron transfer may increase electrical recovery without producing a proportional increase in total COD removal.

Table 3. COD removal and power from pilot-scale MFCs treating real wastewater and laboratory CP-modified MFCs

System & Scale	WW Type	COD Removal (%)	Power Output	HRT	CE (%)	Citations
850-L air-cathode MFC (17 brush modules), no CP	Real domestic-type wastewater	$49 \pm 15\%$ (MFC alone); $91 \pm 6\%$ (MFC + biofilter)	$0.46 \pm 0.35 \text{ W average}$; 0.043 W m^{-2} anode	12 h	~9%	[37]
1000-L modular MFC (GAC), no CP	Real municipal wastewater	70–90%; effluent $<50 \text{ mg L}^{-1}$	$7\text{--}60 \text{ W m}^{-3}$ with real municipal wastewater; 125 W m^{-3} with artificial wastewater	2 h	41–75%*	[38]
1500-L MFC, no CP	Real municipal wastewater	~91%; effluent $\sim 25 \text{ mg L}^{-1}$	$\sim 0.41 \text{ W m}^{-3}$	5 h	N/R	[40]
720-L stacked MFC with metal-oxide cathode/anode catalysts	Real sanitary wastewater	$78.45 \pm 19.12\%$ at 18 h; $87.29 \pm 7.28\%$ at 36 h	0.36 W m^{-3} ; 61 mW maximum	18–36 h	N/R	[39]
226-L air-cathode MFC with AEM, no CP	Real municipal wastewater	31–58%	$0.072\text{--}0.51 \text{ W m}^{-3}$	9–42 h	~15%	[41]

System & Scale	WW Type	COD Removal (%)	Power Output	HRT	CE (%)	Citations
PANInf@carbon cloth, 14-mL laboratory MFC	Acetate buffer	N/R	1,091 mW m ⁻²	Batch	N/R	[9]
PPy/MXene@GF, laboratory MFC	Acetate-based synthetic substrate	N/R	264 mW m ⁻² ; OCV 281 mV	Batch	N/R	[14]
PEDOT@GF, laboratory MFC	POME	COD removal: not reported. Kang et al. [15] reported 3.5 A m ⁻² maximum current density and 51% Coulombic efficiency with POME wastewater	3.5 A m ⁻² maximum current density	N/R	51%	[15]

Abbreviations: AEM, anion-exchange membrane; CE, Coulombic efficiency; COD, chemical oxygen demand; GF, graphite felt; GAC, granular activated carbon; HRT, hydraulic retention time; MFC, microbial fuel cell; N/R, not reported; OCV, open-circuit voltage; POME, palm oil mill effluent; PPy, polypyrrole; PANI, polyaniline; PEDOT, poly(3,4-ethylenedioxythiophene); WW, wastewater.

Critical synthesis and research priorities

The evidence reviewed here supports the following bounded conclusions. CP modification of MFC anodes can produce measurable improvements in electrochemical performance under controlled laboratory conditions, and the magnitude of improvement is consistently dependent on electrode architecture, polymer morphology, composite components, substrate, inoculum, and reactor configuration — not on any single polymer property. Notably, composite systems (PPy/MXene, S-MXene/PPy, PEDOT/MnO₂) consistently outperform single-polymer modifications, demonstrating that the architecture as a whole, rather than the CP alone, often drives the reported gains. For example, the PPy/MXene-modified GF anode reported by Batool et al. [14] produced 264 mW m⁻² compared with 45 mW m⁻² for bare GF, corresponding to approximately a 5.9-fold increase under the conditions of that study. Ahmed and Kim [9] reported a 73% increase in current density for polyaniline nanofibers relative to flat PANI, while the maximum power density increased by approximately 40%, from 777 to 1,091 mW m⁻².

Across polymer types, the available evidence supports the following evidence hierarchy: anode electrochemical performance (high-confidence, matched controls), biofilm enhancement (moderate confidence, correlative), CP-specific EET mechanism (low confidence, proposed/inferred), long-term stability (low confidence, not directly demonstrated in MFCs), and real-wastewater superiority over unmodified electrodes (not yet demonstrated). These results should not be interpreted as evidence that CPs have already demonstrated superiority under wastewater-treatment conditions at practical scale. The strongest available pilot-scale benchmark remains the 850-L air-cathode MFC reported by Rossi et al. [37], which treated domestic-type wastewater for more than six months without CP modification. This provides an important scale-and-real-wastewater benchmark, although direct comparison with laboratory CP studies is inappropriate unless reactor configuration, substrate, electrode-area normalization, HRT, inoculum, and operating conditions are matched.

Conclusions and research priorities

Based on the evidence reviewed, the following conclusions are warranted: CP modification demonstrably improves MFC anode electrochemical performance under controlled laboratory conditions. Performance improvements are system-dependent and frequently attributable to composite architecture rather than the CP alone. Attribution of improvement to the polymer alone is therefore not justified for these systems. CP-specific enhancement of extracellular electron transfer remains incompletely demonstrated. Current evidence is correlative (EIS, biofilm abundance, 16S rRNA sequencing) rather than mechanistic. Long-term polymer stability under MFC operating conditions is a critical evidence gap. Dedoping, delamination, and over-oxidation are established degradation pathways from materials-level studies, but no reviewed study quantified CP conductivity retention, coating adhesion, and electrochemical performance simultaneously over multi-month MFC operation with real wastewater. Real-wastewater performance advantages of CP-modified electrodes over unmodified controls remain undemonstrated at pilot scale. No pilot-scale CP-modified MFC system was identified in the reviewed literature. Cross-study performance ranking is not scientifically justified. Standardized CP-MFC testing protocols specifying at minimum reactor type, electrode area, normalization basis, substrate composition, HRT, operating temperature, and reporting duration are a prerequisite for meaningful cross-study comparison. Economic and practical feasibility data are insufficient for decision-making. No reviewed study reported cost per electrode area or cost per unit of additional power generated for any CP system. The next stage of CP research should therefore move beyond isolated maximum-power-density demonstrations toward standardized, long-duration, real-wastewater comparisons. Future studies should simultaneously quantify electrochemical performance, COD removal, Coulombic efficiency, microbial-community changes, polymer stability, electrode adhesion, material cost, and energy recovery under matched operating conditions. Such studies would provide the evidence needed to determine whether the laboratory advantages repeatedly reported for PANI, PPy, PEDOT, and their composites can be retained during continuous wastewater treatment and translated into practically relevant MFC systems.

Conflict of interest

The authors declare that they have no known financial or personal conflicts of interest that could have influenced the work reported in this manuscript.

Artificial intelligence (AI) use statement

Artificial intelligence (AI)-based tools were used only for language editing, grammar correction, and improvement of readability and clarity during the preparation of this manuscript. The authors independently reviewed, verified, and approved all scientific content, interpretations, references, and final text. AI tools were not used to generate or fabricate experimental data, results, or references.

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