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Review

Microbial Electrosynthesis: The Future of Next-Generation Biofuel Production – A Review

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Abstract

Microbial electrosynthesis (MES) has emerged as a promising bio-electrochemical technology for sustainable CO_2 conversion into valuable organic compounds. This review synthesizes advancements in MES from 2010 to 2025, focusing on electrode materials, microbial communities, reactor engineering, performance trends, techno-economic evaluations, and future challenges, especially on the results reported between 2020 and 2025. Recent innovations in electrode materials, such as conductive polymers and metal–organic frameworks, have enhanced electron transfer efficiency and microbial attachment, leading to improved MES performance. The development of diverse microbial consortia has expanded the range of products achievable through MES, with studies highlighting the importance of microbial interactions and metabolic pathways in product formation. Advancements in reactor design, including continuous-flow systems and membrane-less configurations, have addressed scalability issues, enhancing mass transfer and system stability. Performance metrics, such as current densities and product yields, have significantly improved, demonstrating the potential of MES for industrial applications. Techno-economic analyses indicate that while MES offers promising economic prospects, challenges related to cost-effective electrode materials and system integration remain. Future research should focus on optimizing microbial communities, developing advanced electrode materials, and designing scalable reactors to overcome existing limitations. Addressing these challenges will be crucial for the commercialization of MES as a viable technology for sustainable chemical production

Keywords: microbial electrosynthesis; CO_2 conversion; electrode materials; microbial communities; reactor engineering; performance trends; techno-economics; sustainability; bio-electrochemical systems; renewable energy

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1. Introduction

The Microbial electrosynthesis (MES) is a bio-electrochemical approach that uses microorganisms as biocatalysts to convert CO_2 and electrons (from a cathode) into multi-carbon organic compounds such as acetate, ethanol, butyrate and medium-chain fatty acids. The process was introduced and demonstrated by Nevin et al. in 2010, who showed *Sporomusa ovata* converting CO_2 to acetate on a cathode with high coulombic efficiency, thereby establishing the core MES paradigm: a polarized cathode supplies electrons, electro-trophic microbes fix CO_2 (commonly via the Wood–Ljungdahl pathway), and products are excreted to the bulk medium [1].

Between 2010 and about 2019 MES developed gradually —moving from a proof-of-concept toward improved electrode designs and mixed-culture demonstrations (notable step increases in productivity were already reported around 2015) — but the field's expansion accelerated markedly after 2020 as innovations in electrode materials, sequencing-enabled microbiome analyses, reactor engineering, and early techno-economic modelling converged. The period 2020–2025 therefore represents an intensely productive window for MES research and is the focus of the sections below [2,3].

At its core, MES relies on three interlinked elements:

- **Electrode–microbe electron transfer.** Electrons originate at a cathode (driven by an external power source, preferably renewables). Electron transfer mechanisms include (a) direct extracellular electron transfer (EET) via conductive biofilms or redox proteins, and (b) indirect hydrogen-mediated transfer, wherein electrochemically produced H_2 is consumed by hydrogenotrophic acetogens. Distinguishing between these pathways remains a major experimental and conceptual theme across 2010–2025 studies [1,4].
- **Electro-trophic metabolism**. Many acetogens (e.g., *Sporomusa*, *Acetobacterium*, *Clostridium*) deploy the Wood–Ljungdahl pathway to fix CO_2 to acetyl-CoA and then excrete acetate or reduce further to ethanol/butanol under specified conditions. Advances in metabolic understanding and synthetic biology approaches to expand product scope have intensified after 2020 [5,6].
- **System design**. Reactor architecture, cathode material and geometry, operational potential, pH, mass transfer and anode chemistry jointly determine rates, titers and selectivity. From the initial graphite electrodes (2010) to engineered 3-D printed cathodes, materials and reactor choices have been central to MES progress [1,7].

Figure 1 is showing a schematic image of MES fundamentals which includes: cathode, microbes (biofilm), CO_2 feed, products, anode, and possible electron pathways

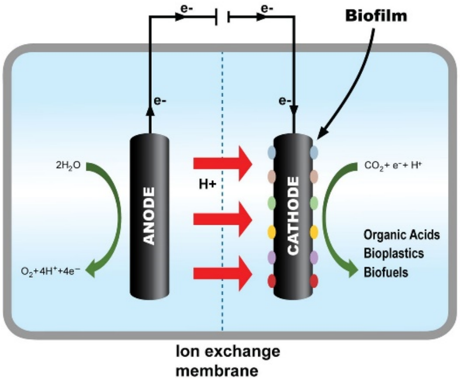

Figure 1. MES fundamentals.

There are several complementary drivers which produced an acceleration of MES research, production and performance gains post-2020 such as: **materials and manufacturing advancements for the electrodes** (graphene, 3-D printing, composites): Carbon nanomaterials, conductive polymers and additive manufacturing enabled cathodes with higher surface area, better mass transfer and improved microbial colonization. Researches undergone mainly in 2023–2024 consolidated these developments and highlighted reproducible productivity increases tied to advanced cathode materials [7,8], **microbiome and sequencing:** paper [9] is a meta-analysis which synthesized 22 MES studies and revealed a conserved cathodic core microbiome (e.g., *Desulfovibrio*, *Acetobacterium*, *Methanobacterium*), showing that operational levers (inoculum pre-treatment, potential, pH) systematically shape community outcomes and product selectivity. This enabled a new focus on community steering and bioaugmentation strategies [9], **systems and TEA:** as electrode and microbiome science matured, investigators began publishing more techno-economic and modelling work — mapping cost drivers, scale-up bottlenecks and niche markets (e.g., specialty chemicals, point-source CO_2 valorization), making MES of greater interest to engineering and policy communities [10,11].

Figure 2 is showing the growth in published papers on MES subject while highlighting the key milestone years

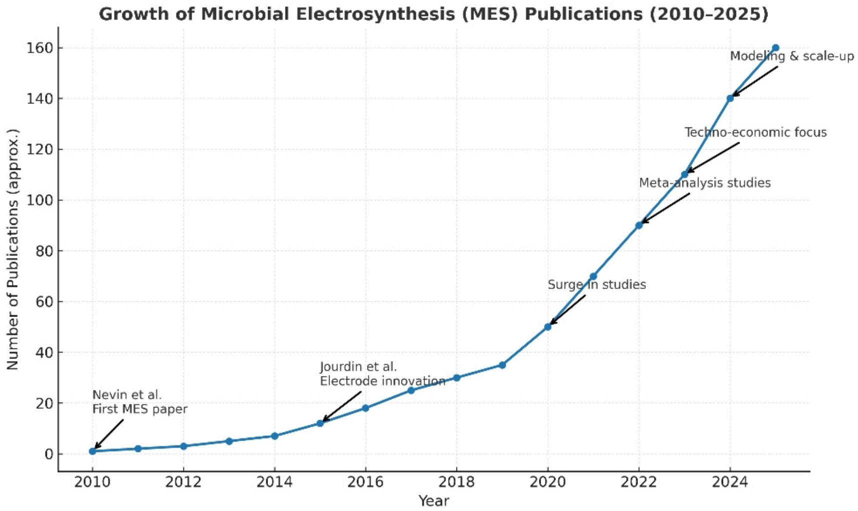

Figure 2. Publication timeline (2010–2025) showing growth in number of MES publications and key milestone years.

Electrode design has advanced **from** plain graphite and carbon felts to sophisticated, engineered cathodes from early era (2010–2016) when was mostly graphite plates, carbon felt, and reticulated vitreous carbon were common supports; micro- and macro-porosity, and simple conductive coatings were used to increase biofilm formation and reduce internal resistances [1,2], **towards** transitional improvements 2017–2019 by incorporating carbon nanotubes and hierarchical porous coatings improved areal productivity and biofilm development (benchmarks established prior to the 2020 surge) [12] and **finally** reaching rapid innovation 2020–2025 by achieving complex architecture like graphene / rGO and carbon-based 3-D architectures. Multiple reports [7,13] but especially [7] detail how graphene derivatives and 3-D printed carbon aerogels increase interface conductivity and biofilm compatibility (improving both startup and steady-state rates).

Metal oxide coatings emerged when catalyst layering was introduced (including Ni, MoS_2, CoP, and oxide coatings) to tailor hydrogen evolution and lower overpotentials, balancing microbe-friendly H_2 production with direct electron transfer. Recent catalyst-assisted studies [14,15] evaluate Ni- and transition metal-based modifications for higher acetate yields.

Nowadays there are biocompatible bimetallic oxide coatings such as $MnFe_2O_4$ coatings that substantially increased acetate areal productivity and supported *Acetobacterium* enrichment — one of the most significant material-driven performance jumps in the 2020s and additive manufacturing / 3-D printed electrodes which enabled bespoke lattice structures that optimize mass transfer, conductivity and biofilm penetration, showing dramatic performance improvements in scaled lab reactors [17].

Figure 3 is showing a comparative chart between different cathode types, from graphite to Fe-Mn coated one.

Moreover, intensive researches have been made towards understanding and engineering the cathodic **microbiome** which is central for selectivity and stability. Thus, [22] synthesized several studies and found an ~80% overlap in a cathodic core community across acetogenic and methanogenic systems — an observation that provided a predictable foundation for community manipulation (bioaugmentation, pretreatment, potential control) [9]. Since 2020, multiple groups reported that seeding with acetogens (e.g., *Acetobacterium*, *Clostridium* spp.) or using selective pre-treatments (heat, chemical inhibitors) can bias communities toward acetogenesis and reduce methane formation. Operational variables (pH, potential, H_2 partial pressure) remain powerful levers to maintain acetogen dominance. [3,4] and recent perspectives advocate and begin to demonstrate the use of engineered pure cultures and edited pathways to expand products beyond acetate (toward butyrate, caproate, alcohols), while improving EET capabilities and tolerance to electrochemical conditions [5,6].

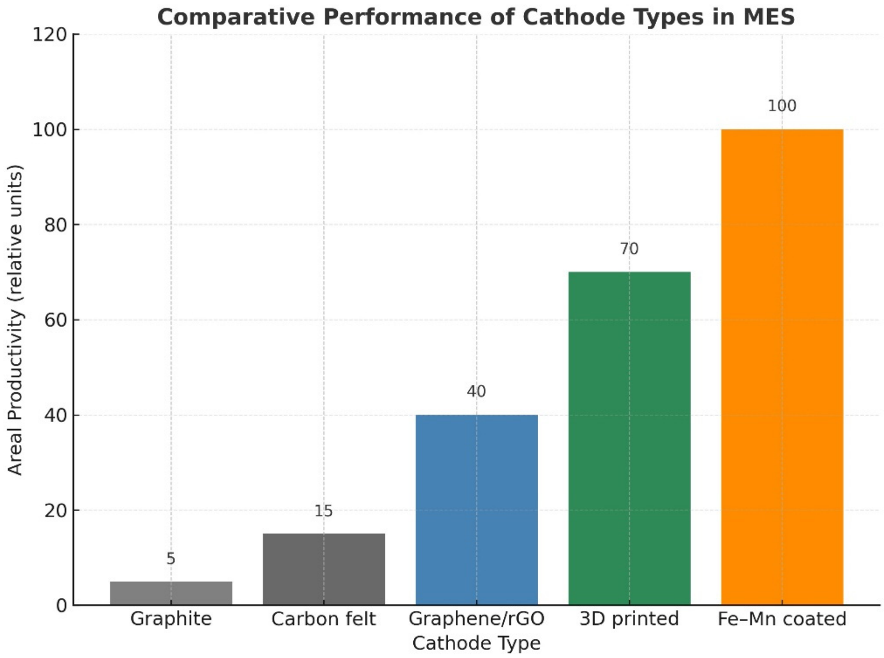

Figure 3. Comparative performance chart of cathode types (graphite, carbon felt, rGO/graphene, 3-D printed, Fe–Mn coated.

Another important aspect related to MES is **reactor engineering** & **system configurations** because it sums system-level engineering mass transfer, electrode spacing, gas handling, and product separation. There are several critical aspects that must be taken into consideration when designing a MES reactor: *flow electrodes and stacked reactors* demonstrated higher titers (e.g., reports of several g L^{-1} acetate in flow systems), suggesting scale-friendly concepts that improve gas and liquid mass transfer [18]. Alternative cell designs that improve CO_2 availability to biofilms (*gas diffusion cathodes*) *or* use *salinity* gradients for driving current have been explored, showing system gains in productivity and coulombic efficiency. [8] mathematical *models and control* strategies developed between 2021–2025 now allow optimization of potential, flow, and H_2 evolution rates to predict productivity and scale behavior, illuminating pathways for pilot reactors [19].

2. Evolution of Electrode Materials for Microbial Electrosynthesis

2.1. Carbonaceous Materials and Graphene-Based Electrodes

From 2010–2015, MES cathodes were dominated by **graphite plates, carbon felt, reticulated vitreous carbon, and carbon papers** because they were inexpensive, chemically stable, and biocompatible for acetogenic biofilms. Performance increases in this period mainly came from enlarging surface area and improving roughness to favor biofilm attachment and reduce ohmic losses. Subsequent reviews and historical perspectives document this early reliance on porous carbons and the pivotal role of surface morphology in accelerating start-up and boosting electron transfer to acetogens [20,21].

From ~2016 onward, **graphene and graphene-derivative** cathodes—reduced graphene oxide (rGO), graphene aerogels, and graphene-polymer blends—rapidly entered MES. Graphene's high conductivity, tunable surface chemistry, and ability to form hierarchical 3-D networks improved both direct extracellular electron transfer and **controlled H_2-mediated** routes by enhancing local electron density and biofilm density. Dedicated reviews synthesize dozens of reports showing that graphene coatings and graphene-based composites systematically increase current density, coulombic efficiency, and acetate/MCFA productivities, compared with unmodified felt or plate electrodes [22].

A parallel trend in the 2020s is **circular-carbon electrodes**—biochar and waste-derived carbons (including algal-derived frameworks)—which deliver high porosity, wettability, and microbe-compatible functionalities at low cost. Recent studies show that tailoring pore architecture and oxygen-containing groups in such carbons improves colonization and durability, while maintaining performance near that of engineered graphene—an attractive direction for scale-up [7,23].

2.1.1. Advantages and Disadvantages on Using Carbonaceous and Graphene-Based Electrodes in MES

Advantages

- Carbonaceous electrodes (graphite, felt, RVC, paper): Low cost, scalable, chemically stable, and relatively easy to modify.
- Graphene-based electrodes: Outstanding conductivity, hierarchical porosity, tunable surface chemistry, and superior performance in terms of electron transfer and product selectivity.
- Circular-carbon electrodes: Sustainable, low-cost, derived from biomass or waste; high porosity and surface functionalization enable strong microbial adhesion and long-term durability.

Disadvantages

- Plain carbon electrodes: Limited conductivity compared to advanced materials; poor catalytic activity toward hydrogen evolution, requiring high applied potentials.
- Graphene-based: High cost of synthesis, difficulties in large-scale and reproducible fabrication, and potential instability under prolonged operation.
- Circular carbons: High variability in structure and performance depending on feedstock and processing conditions; often lower conductivity than engineered graphene-based.

2.1.2. Gaps and Challenges on Using Carbonaceous and Graphene-Based Electrodes in MES

Despite clear advances, several challenges remain: i) Scalability: Transitioning from lab-scale felts and coatings to industrial-scale electrodes remains uncertain, particularly for graphene-based systems, ii) Durability: Long-term stability under continuous operation (biofilm detachment, surface fouling, or structural collapse) remains poorly understood, iii) Mechanistic understanding: The interplay between electrode surface chemistry, electron transfer pathways, and microbial community dynamics is not fully resolved, iv) Circular carbon standardization: Lack of standardized processing and characterization methods makes cross-comparison between studies difficult.

2.1.3. Future Perspectives on Using Carbonaceous and Graphene-Based Electrodes in MES

- Hybrid electrodes: Combining biochar/circular carbons with thin graphene or catalytic skins may achieve both cost-effectiveness and high performance.
- Scalable manufacturing: Techniques such as 3D printing and roll-to-roll coating can bridge lab innovation with industrial feasibility.
- Functionalized surfaces: Rational tuning of oxygen groups, nitrogen doping, or heteroatom functionalization could steer microbial adhesion and selectivity.
- Integration with techno-economics: Future studies should assess not only performance metrics (current density, coulombic efficiency) but also life-cycle impacts and cost per unit product.

Table 1 is showing the above-mentioned aspects in an easier to read way.

Electrode Type	Advantages	Disadvantages	Gaps/Challenges	Future Perspectives
Carbonaceous (graphite, felt, paper, RVC)	- Low cost, abundant, scalable- Chemically stable- High surface roughness → good	- Limited conductivity- Low intrinsic catalytic activity (HER)-	- Need improved catalytic function- Limited long-term durability data-	- Surface functionalization (doping, coatings)- Integration with conductive

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	biofilm attachment- Easy to modify with catalysts	Require high applied potentials	Scaling issues for high productivity	polymers- Engineering 3D structured carbons
Graphene-based (rGO, aerogels, composites)	- Exceptional conductivity- Hierarchical porosity improves mass transfer- Tunable chemistry (functional groups)- Enhanced electron transfer & product selectivity	- High synthesis cost- Scale-up remains difficult- Potential instability during long-term runs	- Lack of standardized fabrication methods- Limited understanding of graphene–microbe interactions- Reproducibility concerns across labs	- Hybrid electrodes (graphene + biochar)- Roll-to-roll or scalable coating methods- Use in advanced 3D printed cathodes
Circular carbons (biochar, waste-derived)	- Sustainable & low-cost- Derived from biomass or waste (circular economy)- High porosity & wettability- Comparable biofilm colonization to graphene	- Variability in properties (feedstock dependent)- Often lower conductivity than graphene- Inconsistent performance across studies	- Lack of standardization in feedstock processing- Limited comparative benchmarks with engineered electrodes	- Standardized production methods- Hybridization with conductive nanomaterials- Scalable sustainable electrodes for industrial MES

2.2. Composite Electrodes (Carbon + Polymers/Metals/Catalysts)

As the field matured, researchers shifted from "plain carbon" to **composite cathodes** that combine a conductive carbon backbone with electrocatalysts or conductive polymers to manage interfacial kinetics and **in-situ H_2 evolution**. Since ~2020, three families have stood out: i) **3-D printed carbon lattices** (often Ni/Mo-modified) that fine-tune H_2 delivery and mass transfer. Carefully engineered lattice topologies (cubic, diamond, Schwarz, etc.) and catalytic skins improve local H_2 availability to acetogens and dramatically raise volumetric production rates in bio-electrochemical CO_2-to-organics systems [17,24], ii) **Conductive polymer composites**—for example, commercially available conductive ABS/PLA lattices or poly-pyrrole/polyaniline coatings—used either as the whole scaffold or as surface modifiers. Studies with **electrically conductive polymer lattices** (sometimes further **Ni-functionalized**) report stable acetate and methane production while offering low-cost, manufacturable structures; they also reveal trade-offs between polymer conductivity, mechanical integrity, and long-term biocompatibility [25]. iii) **Catalyst-assisted carbon cathodes** (Ni, Cu, Fe, Co, Mo, perovskites). These composites lower overpotentials for HER, enabling a **microbe-friendly H_2 flux** without damaging local pH, and improve coulombic efficiencies to acetogenesis when the potential is carefully regulated. Newer work evaluates **Fe, Cu, Ni** surfaces in side-by-side tests for CO_2-to-acetate MES, clarifying how catalyst identity steers selectivity and biofilm composition [26,27].

2.2.1. Advantages and Disadvantages on Using Composite Electrodes

Advantages

- 3D printed carbon lattices (Ni/Mo-modified): Their engineered porosity and topology provide enhanced mass transfer and fine-tuned H_2 delivery to microbial biofilms. Studies show

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significantly increased volumetric productivities, particularly for acetate, due to the localized control of hydrogen flux near acetogens [Jourdin et al., 2021; Hou et al., 2024].

- Conductive polymer composites (poly-pyrrole, polyaniline, conductive PLA/ABS): These materials are low-cost, easily manufacturable, and mechanically flexible, enabling scalable electrode designs. Polymers also offer a tunable surface chemistry that supports microbial adhesion. Hybrid polymer-metal composites have reported stable long-term operation for acetate and methane production [19,21,25].
- Catalyst-assisted cathodes (Ni, Cu, Fe, Co, Mo, perovskites): The incorporation of catalytic coatings lowers HER (hydrogen evolution reaction) overpotentials and provides a controlled, microbe-friendly H_2 flux, avoiding damaging local alkalinization. This leads to higher coulombic efficiencies and improved selectivity toward acetate and other reduced compounds [14,19–21].

Disadvantages

- 3D printed lattices require specialized manufacturing and may suffer from structural brittleness after prolonged use.
- Conductive polymers often face trade-offs between electrical conductivity and mechanical stability; their long-term bio-compatibility in harsh electrochemical environments is still under debate.
- Metal catalysts risk ion leaching, which can be toxic to microbial communities, and can increase system costs.

2.2.2. Gaps and Challenges on Using Composite Electrodes

Several unresolved issues persist in the development of composite electrodes: i) Standardization: Results vary widely due to differences in synthesis methods, surface treatments, and testing protocols, ii) Durability: Few studies evaluate electrode performance over thousands of operational hours, a requirement for industrial adoption, iii) Biofilm–electrode interactions: The impact of catalyst type or polymer chemistry on microbial community assembly and metabolic activity remains underexplored, iv) Economic scaling: While high-performing in the lab, composites often involve costly metals or polymers that raise questions of economic feasibility.

2.2.3. Future Perspectives on Using Composite Electrodes

To move MES closer to commercialization, future research should prioritize:

- Hybrid electrodes: Combining biochar or other circular carbons with thin catalytic coatings (Ni, Fe, Co) to balance performance and cost.
- Advanced manufacturing: Adoption of 3D printing, laser etching, and roll-to-roll coating for scalable, reproducible electrodes.
- Eco-friendly catalysts: Replacement of noble or heavy metals with earth-abundant, biodegradable alternatives (e.g., Fe- or Mn-based composites).
- Integrated techno-economic analysis: Studies should pair electrode innovations with LCA (life-cycle assessment) and cost modeling to assess true scalability.

Table 2 is showing the above-mentioned aspects in an easier to read way.

Composite Electrode Type	**Advantages**	**Disadvantages**	**Gaps/Challenges**	**Future Perspectives**
3D Printed Carbon Lattices (Ni/Mo,	- Tailored 3D geometry for high surface area & mass transfer- Enhanced localized H_2 delivery	- Requires specialized equipment- Mechanical brittleness under	- Limited durability testing (>1000 h)- Lack of standard print protocols-	- Scale-up via industrial 3D printing- Hybridization with low-cost biochars-

doped carbons)	to biofilms- High productivities for acetate & other products	long-term use- Fabrication costs still high	Scale-up feasibility unproven	Integration into modular reactor stacks
Conductive Polymers (poly-pyrrole, polyaniline, PLA/ABS blends)	- Low-cost & lightweight- Flexible, scalable manufacturing- Tunable chemistry enhances microbial adhesion- Good long-term stability in some studies	- Moderate conductivity compared to metals- Mechanical degradation in harsh electrochemical environments- Potential bio-compatibility concerns	- Limited reproducibility between labs- Unknown long-term chemical resistance- Need more data on polymer–biofilm interactions	- Polymer-metal or polymer-carbon hybrids- Development of biodegradable conductive polymers- Use in flexible/portable MES reactors
Catalyst-Coated Cathodes (Ni, Fe, Cu, Co, Mo, perovskites)	- Lower HER overpotentials- Controlled H_2 flux prevents pH shocks- Increased coulombic efficiency and selectivity	- Risk of metal ion leaching (microbial toxicity)- Added costs (especially noble/perovskite catalysts)- Complex synthesis routes	- Few studies on biofilm community shifts under catalysts- Insufficient life-cycle & cost analyses- Variability in coating adhesion & durability	- Earth-abundant catalysts (Fe, Mn)- Thin catalytic coatings over low-cost supports- Techno-economic integration with renewable energy systems

2.3. Bimetallic Oxide Cathodes

The latest wave (2023–2025) introduces **bimetallic oxides** on carbon supports to couple high conductivity with redox-active, microbe-compatible surfaces. A notable example is **Fe–Mn spinel-type oxides** (e.g., $MnFe_2O_4$) deposited onto carbon felt: reports in 2024 describe substantially **higher acetate areal productivities**, faster start-up, and an enrichment of acetogenic taxa (e.g., *Acetobacterium*), compared with uncoated controls—attributed to balanced HER kinetics, improved charge transfer, and favorable surface chemistry for biofilm nucleation [28].

These oxide coatings are attractive because they **stabilize interfacial pH** and **buffer redox** conditions, mitigating local extremes that can detach biofilms. Their modularity also allows tuning oxygen vacancies and metal ratios to match desired HER rates for acetogen uptake. Early demonstrations rely on lab-scale felts, but the chemistry is compatible with roll-to-roll coating—suggesting a path to durable, scalable cathodes if adhesion and fouling can be controlled over thousands of hours [16].

2.3.1. Advantages and Disadvantages on Using Bimetallic Oxide Cathodes

Advantages

- Synergistic catalysis: Combining two or more metals enhances electron transfer kinetics and lowers overpotentials compared to monometallic oxides.
- Abundance and sustainability: Many BMOs (Fe, Mn, Ni-based) are earth-abundant, low-cost, and environmentally benign compared to noble metals.

- Enhanced biofilm performance: Oxide surfaces offer hydrophilicity, tunable porosity, and surface oxygen groups that promote microbial adhesion and stable electro-trophic growth.
- Selectivity: BMOs can regulate H_2 evolution to match microbial uptake rates, avoiding accumulation and energy losses.

Disadvantages

- Conductivity issues: Many oxides have lower intrinsic conductivity compared to carbon or graphene, requiring support materials or dopants.
- Metal leaching: Prolonged use may release ions (e.g., Ni^{2+}, Co^{2+}), potentially toxic to microbial communities.
- Complex synthesis: Hydrothermal, sol-gel, or electrodeposition methods can be costly and difficult to scale.
- Variability: Performance is highly dependent on metal ratios, synthesis conditions, and electrode architecture.

2.3.2. Gaps and Challenges on Using Bimetallic Oxide Cathodes

Despite clear advances over the previous two types, several challenges remain: i) Mechanistic clarity: The precise role of BMOs in balancing direct electron transfer vs. H_2-mediated pathways remains underexplored, ii) Durability: Long-term stability (>3000 h) under continuous operation is rarely demonstrated, iii) Standardization: Few comparative studies exist across different BMO compositions under identical MES conditions, iv) Integration: Limited techno-economic assessments exist for industrial application of BMOs.

2.3.3. Future Perspectives on Using Bimetallic Oxide Cathodes

- Low-cost synthesis: Emphasis on scalable, eco-friendly methods (e.g., electrodeposition on felts, waste-derived metal oxides).
- Hybrid electrodes: Combination of BMOs with graphene or biochar supports to overcome conductivity limitations.
- Mechanistic studies: In situ spectroscopy and omics approaches could resolve how BMOs interact with electro-trophic consortia.
- Circular economy approaches: Utilizing waste streams (steel slag, mine tailings) as oxide precursors to reduce costs.

Table 3 is showing the above-mentioned aspects in an easier to read way.

Electrode Type	Advantages	Disadvantages	Gaps/Challenges	Future Perspectives
Biometallic Oxides (Fe–Mn, Ni–Co, Cu–Fe, perovskites)	- Synergistic catalytic activity- Earth-abundant, low-cost metals- Hydrophilic, biofilm-friendly surfaces- Tunable HER selectivity	- Low intrinsic conductivity- Risk of metal ion leaching (toxicity)- Complex & costly synthesis- Performance highly condition-dependent	- Limited long-term stability data- Lack of standardized testing- Poor understanding of electron transfer mechanisms- Few techno-economic studies	- Hybrid electrodes with carbon/graphene supports- Scalable electrodeposition or waste-derived oxides- Mechanistic in situ studies- Integration with circular economy feedstocks

2.4. Cross-Cutting Insights on the Development of MES Electrodes as Resulting from 2010–2025 Literature

Across these families, two principles recur. First, **hierarchical porosity + high conductivity** (graphene, aerogels, printed lattices) correlate with faster colonization and higher steady-state currents. Second, **catalytic moderation of HER** (metals/oxides) is essential to couple electrochemistry with microbial uptake: too little H_2 limits rates; too much shifts communities toward methanogenesis or causes pH spikes. Recent studies formalize this by **voltage/H_2-flux control**, stabilizing acetate production over long runs [4].

Looking ahead, the most promising cathodes combine **sustainable carbons (biochar/graphene hybrids)** with **thin catalytic skins (Ni, Fe–Mn spinel, perovskite)** on **engineered 3-D architectures**. Such designs aim to deliver low cost, high durability, and field-scale manufacturability while preserving the microenvironments mesophilic acetogens require [7,17].

3. Evolution of Microbial Communities and Biofilm Engineering

Microbial electrosynthesis (MES) relies on cathodic biofilms that reduce CO_2 to organics using electrons supplied by a solid electrode, either directly (DET) or indirectly via H_2/format (MET). Since 2010, cathode material design and operating strategies have progressively shifted from inert carbons toward graphene-modified carbons, composites, and bi-metallic oxides, each reshaping biofilm structure, community assembly, and electron-transfer modes. Early MES studies on graphite felt/paper and carbon cloth consistently enriched acetogenic biofilms (e.g., *Acetobacterium*, *Sporomusa*) and co-occurring hydrogenogenic partners such as *Desulfovibrio*, establishing the canonical view that H_2-mediated CO_2 reduction dominates under most operating regimes. Recent meta-analyses quantify this picture, showing that acetogenic and methanogenic MES share ~80% of a "cathodic core microbiome," with inoculum pre-treatments and set potentials steering community outcomes and the (re)emergence of methanogens over time. These data also implicate Desulfovibrio as an early H_2 initiator that supports *Acetobacterium* or *Methanobacterium* depending on conditions [9,28].

3.1. Carbonaceous Materials & Graphene

Unmodified carbon felts/RVC remain workhorses because of their biocompatibility, roughness, and cost; they reliably host thick acetogenic biofilms and tolerate the alkaline microenvironments associated with vigorous HER. Yet their limited intrinsic catalytic activity means higher overpotentials and slower start-up when H_2 supply is rate-limiting. Surface engineering with graphene and reduced graphene oxide (rGO) has therefore become a central biofilm-engineering strategy. Graphene coatings/aerogels raise conductivity, provide hierarchical porosity for CO_2 delivery, and present functional groups that improve attachment, collectively boosting electron transfer, coulombic efficiency, and product selectivity (e.g., acetate) compared with bare carbon felts. Recent focused reviews emphasize that graphene-modified cathodes increase bacterial loading and biofilm continuity, while also noting scale-up and cost challenges (agglomeration, reproducibility, fabrication). Multiple bench studies show rGO-modified felts producing denser, more electroactive biofilms and better selectivity [22,29].

3.2. Composite Electrodes

From ~2020 onward, composites—carbon scaffolds integrated with metals, alloys, or conductive polymers—have accelerated progress by engineering the H_2 micro-niche at the biofilm–electrode interface. 3D-printed carbon aerogels plated with Ni–Mo exemplify this shift: by distributing large currents over high surface area at low local current density, they stabilize start-up, minimize bubble disruption, and sustain near-quantitative conversion in electro-methanogenesis models; analogous principles are now applied for acetogenic MES. These electrodes effectively tune H_2 generation to match microbial uptake, which promotes stable acetogenic or methanogenic biofilms with high coulombic efficiency. Parallel work with conductive polymer composites and nickel-foam-decorated felts similarly reports higher titers via improved in situ H_2 delivery and durable biofilm architectures [24].

Community-wise, composites tend to narrow the functional guilds near the cathode by providing steadier electron donors (H_2) and more uniform shear/porosity, enriching Acetobacterium in acetogenic cells or Methanococcus/Methanobacterium in electro-methanogenesis, while maintaining supportive fermenters and sulfur cycle shuttles (e.g., Desulfovibrio). Reviews of cathode materials underscore that such material-driven biogeography is as decisive as inoculum choice for steering communities away from parasitic methanogenesis when acetate or longer-chain acids are targeted [30].

3.3. Bi-Metallic Oxides (BMOs)

Bi-metallic oxides (e.g., Fe–Mn, Co–Ni, spinel/perovskites) emerged strongly after 2020 as earth-abundant HER catalysts that are biofilm-friendly. Recent studies show Fe–Mn oxide–modified cathodes are biocompatible and electroactive, enabling efficient CO_2-to-acetate conversion while supporting stable acetogenic biofilms; Co–Ni on carbon felt has achieved high faradaic efficiencies to acetate/ethanol with robust biofilm formation. Mechanistically, BMOs lower HER overpotentials, moderate local pH, and present hydrophilic oxide surfaces that can boost extracellular polymeric substance (EPS) formation and cell adhesion, thereby balancing DET/MET pathways in mixed cultures. Earlier work with Fe_3O_4/GAC 3D cathodes already highlighted the benefit of magnetite nanoparticles for acetate productivity and biofilm enrichment [16,31,32].

3.4. Gaps and Challenges on Co-Shape Communities

Across materials, set potential, CO_2 supply, and current distribution remain dominant levers: more negative potentials accelerate HER but can favor methanogens, whereas milder potentials and periodic interventions (e.g., headspace flushing, selective inhibitors) help maintain acetogenic dominance. Flow-through architectures and “zero-gap” designs that retain H_2 or distribute it evenly reduce competitive losses and select for target guilds; recent reports demonstrate leaps in areal productivity via improved gas retention and tailored flow paths [28,33].

3.5. Future Perspectives on Biofilm Engineering

The field is converging on material–microbiome co-design: (i) hierarchical carbons/graphene to maximize attachment and electron access; (ii) composites that meter H_2 to biofilms with printable, scalable architectures; and (iii) BMOs to deliver low-overpotential, bio-compatible HER on earth-abundant chemistries. Meta-analysis suggests that sustained suppression of methanogenesis will require repeated operational nudges alongside material design, because community assembly trends stochastically back toward methanogens over time. Future priorities include standardized comparative testing, omics-resolved mechanism mapping of DET vs MET across surfaces, and scale-up studies that couple biofilm durability (≥1000–3000 h) with techno-economics [9].

4. Evolution of Reactor Configurations and Process Engineering

The 2010s began with simple H-cell or dual-chamber reactors (anion/cation exchange membranes, carbon-felt cathodes), later accompanied by membrane-less designs to reduce ohmic losses and parts count. Proof-of-concept studies showed acetate production in membrane-less cells but also highlighted cross-over, oxygen intrusion, and biofilm instability at scale [34]. As the field matured, engineering priorities shifted toward gas management, mass transfer, and current distribution. Since 2022 it was clear that single-chamber membrane-less reactors are generally unsuitable for high-rate MES unless gas separation and pH control are carefully addressed, steering research to flat-plate, directed-flow, and compartmentalized stacks [35].

A notable step was the emergence of directed flow-through/plate reactors that spread current over large, thin electrodes and orchestrate CO_2 delivery across the biofilm. Recent plate-reactor studies report productivities competitive with established biotechnologies, clarifying hydrodynamics, pressure drop, and flow-path design as primary levers [36]. In parallel, zero-gap configurations with extended flow paths have been introduced to retain and consume in-situ H_2

before it escapes, markedly improving conversion to biomethane and offering design lessons that translate to acetogenic MES [33].

4.1. Carbonaceous & Graphene Cathodes: Surface Area, Gas Handling, and GDEs

Reactor advances with carbon felt/paper focused on increasing specific area, lowering ohmic losses, and improving CO_2 supply to thick biofilms. Gas-management features—gas diffusion layers (GDL), microporous layers (MPL), and macroporous substrates (MPS)—migrated from electrochemical CO_2-RR into MES, enabling stable gas–liquid–solid contact while limiting electrolyte flooding [3]. Incorporating graphene/rGO coatings on felt and papers increased conductivity and wettability, enabling denser, more continuous biofilms that tolerate higher areal currents in flow-through plates or stacked cells; comprehensive reactor-design reviews since 2022 capture these material–hydrodynamic interactions [37]. As a bridge to scale, GDE-assisted MES has been repeatedly highlighted for raising areal productivity by reducing boundary-layer limitations and improving CO_2 transfer into the cathode [38].

4.2. Composite Electrodes: Engineering the H_2 Micro-Niche

From ~2020, composite cathodes—carbon scaffolds integrated with metals/alloys or conductive polymers—have been paired with 3D flow architectures to manage where and how fast H_2 is generated. Custom 3D-printed carbon aerogels plated with Ni–Mo demonstrated unprecedented volumetric rates in electro-methanogenesis by tuning H_2 flux via topology and current distribution, an approach now informing acetogenic MES stack design (low local j to prevent bubble detachment; high total j for throughput) [24]. Beyond printing, flow-electrode MES—pumping conductive carbon slurries through the cathode compartment—improves electrode wetting and mass transfer while maintaining reasonable energy efficiency, illustrating a different scale-up route [18]. New biocathode constructs that combine 3D frameworks with catalytic skins report >90% total Faradaic efficiency to C_2 products (acetate/ethanol) by enhancing electron availability and minimizing diffusional dead zones [32].

4.3. Bimetallic Oxides: Low-Overpotential HER and Biofilm Compatibility

A major post-2020 trend is coating carbon scaffolds with earth-abundant bimetallic oxides (BMOs) (e.g., Fe–Mn, Co–Ni) to lower HER overpotentials and stabilize local pH near the biofilm. This process-electrode co-design lets reactors run at milder potentials/voltages while sustaining high areal currents without stripping biofilms via violent gas evolution. Recent studies with Fe–Mn oxides show higher acetate productivities and robust community assembly on flat-plate and felt cathodes; Co–Ni on felt likewise improves conversion and Faradaic efficiency to C_2 products [16]. Reactor reviews now treat catalyst selection and placement as integral to configuration—e.g., thin catalytic skins on flow-through plates vs zero-gap cells—because H_2 residence time and bubble size strongly influence selectivity and coulombic efficiency [37].

4.4. Scale-Up Lessons: Hydrodynamics, Compartmentalization, and Control

Systems-level analyses show that scaling MES demands predictable flow regimes, gas retention, and robust compartments that prevent cross-over while minimizing resistances. Pilot-scale BES literature identifies module-based stacks, short ionic paths, and balanced gas management as universal success factors, aligning with new MES plate and zero-gap designs [39,40]. Finally, process control—regulating potential/voltage and H_2 availability—has emerged as a decisive tool to stabilize acetate synthesis and suppress methanogenesis over long runs, tying operation tightly to reactor hardware [4].

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4.5. Gaps & Limitations on Reactor Configurations and Process Engineering

Despite creative designs (H-cell, membrane-separated flow cells, trickle beds, tubular/plate stacks), insufficient delivery of CO_2 and reducing equivalents to deep biofilm layers caps space–time yields. Even recent productivity gains with compact plate/tubular designs still report gradients of pH, H_2 and CO_2 within porous cathodes that sustain unwanted methanogenesis or limit carboxylate formation, indicating persistent transport non-uniformity at scale [35,41]. Most reactors rely on in situ H_2 as the actual electron carrier; however, H_2 slip to the headspace, short residence times, and poor retention across electrode channels depress coulombic efficiency and selectivity. Zero-gap cells improve ohmic losses but still struggle with H_2 retention and flow distribution unless specifically engineered (extended flow paths, porous flow fields), and sensitivity to membrane hydration/ohmic rise remains [33,42]. Traditional centimeter-scale gaps inflate cell voltages. Zero-gap/BPM configurations lower resistance but introduce new constraints—water management, carbonate crossover, and mechanical compression tolerances—making stable long-term operation nontrivial, especially with real waste streams [42]. Gas-diffusion electrodes (GDEs) and hierarchical carbons enable high interfacial areas, yet they are susceptible to flooding, biofouling, and loss of three-phase contact over time; conducting-polymer retrofits remain promising but not field-proven in long campaigns [38]. Aside from a few studies on stacked/flow-electrode MES and recent plate/tubular prototypes, the literature still lacks month-scale (>1,000 h) runs with stable product slates, full energy balances, and validated cleaning/maintenance cycles. Most techno-economic inferences rest on short-run lab data [18,36]. pH control can suppress methanogenesis, but micro-gradients inside thick felts maintain hydrogenotrophic methanogens; bioaugmentation often fails to persist without matching hydrodynamics and selective pressures [41].

4.6. Future Perspectives on Reactor Configurations and Process Engineering

Plate-type and tubular “zero-dead-volume” reactors with engineered flow fields should be prioritized, since they minimize diffusion distances and enable precise residence-time control. New channel topologies (serpentine, interdigitated) designed by CFD specifically for H_2 retention and uniform shear show clear promise for stabilizing selectivity and raising current density [36]. Treat H_2 as a managed intermediate: (i) design extended/porous flow paths for in-plane retention; (ii) implement headspace recirculation and controlled pressurization; and (iii) integrate micro-sparging or catalytic “H_2 polishing” zones to keep H_2 near the biofilm. Early zero-gap demonstrations indicate that such tactics can sharply improve methane or acetate productivities when coupled to proper flow distribution [33,42]. Pair GDEs with anti-flooding microstructures and breathable binders; explore binder-less, mechanically robust GDEs and conducting-polymer interlayers to maintain three-phase contact and reduce start-up times. Materials advances must be co-designed with cleaning strategies (back-pulsing, periodic polarity tweaks) to extend runtime [38]. Slurry/flow electrodes (e.g., PAC-amended) increase effective surface area and homogenize current distribution in stacks, doubling acetate productivities and improving energy efficiency; translating this into hygienic, low-shedding industrial modules is a near-term engineering task [18]. The highest reported throughputs increasingly pair MES with gas fermentation or chain-elongation steps and employ intensified separation (e.g., electrodialysis) to avoid end-product inhibition. Designing reactors for in-line product extraction and modular coupling will be key to reproducible $>g{\cdot}L^{-1}$ titers and to reach TRL 4–5 [43]. Community shifts, foulants, and inorganic scaling in real matrices require reactors that accommodate online cleaning, membrane re-wetting in zero-gap stacks, and replaceable cathode cassettes. Long-horizon field trials with water/waste CO_2 are urgently needed [6]. Pair continuous sensors (pH, redox, gas composition) with digital twins that couple biofilm growth, electrochemistry, and hydrodynamics; optimize for cost per kg product rather than current density alone. Reviews emphasize the importance of moving beyond H-cells toward controlled, instrumented pilots [7,35].

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5. Performance Trends and Techno-Economic Signals

5.1. Performance Trends

Early 2010s—proof-of-concept. Dual-chamber "H-cell" and membrane-less systems with carbon felt/paper cathodes achieved low areal productivities and modest coulombic efficiencies (CEs), limited by mass-transfer, ohmic losses, and uncontrolled H_2 evolution. Reviews through 2023–2024 such as [3] summarize that these reactors established feasibility but rarely exceeded tens of $g \cdot m^{-2} \cdot d^{-1}$ acetate productivities [3].

Between 2016–2020—materials & gas management emerged on the scene of MES. Graphene-modified/porous carbons and early gas-diffusion approaches pushed current density and CE upward by improving CO_2 supply and biofilm continuity. Empirical thresholds for economic relevance began to appear in TEAs, indicating MES would likely require 50–100 $mA \cdot cm^{-2}$ class cathode current densities to pay off at realistic electricity prices [44].

In early 2020 until 2023—flow-electrode MES with PAC slurries roughly doubled acetate production rates versus static packed felts while keeping energy consumption near 0.02 $kWh \cdot g^{-1}$ (acetate), a meaningful step toward process intensification [8]. Nickel-foam-decorated felts showcased the value of in-situ H_2 delivery, achieving high acetate titers with mixed communities [45].

In last years (2023–2025) —plate/zero-gap reactors and catalytic skins, a new generation of thin plate MES reactors, reported productivities competitive with established biotechnologies, signaling a break from the H-cell era [36]. In parallel, zero-gap cells with extended flow paths improved H_2 retention and markedly enhanced biomethane conversion, highlighting the centrality of hydrogen management to CE and energy efficiency [33]. Bimetallic-oxide or low-cost metal catalysts integrated on carbon scaffolds sustained higher rates by lowering HER overpotential without resorting to precious metals, improving stability in long runs [46].

Record and representative metrics: A synthesis of MES cathode materials collates best-in-class numbers—including $|j| \approx 200$ $A \cdot m^{-2}$ and acetate $\approx 1{,}330$ $g \cdot m^{-2} \cdot d^{-1}$ on advanced biocathodes under optimized conditions—while also noting that these are not yet routine at pilot scale [30]. Single-strain platforms (e.g., *Clostridium ljungdahlii*) demonstrated controllable, high-rate acetate production in well-managed reactors, informing how operation can narrow product variance [5]. Catalyst-assisted MES further tied current density → productivity scaling to controlled H_2 flux and community shifts [26].

Stability via operational control: Voltage/H_2-flux regulation strategies published in 2024–2025 show stabilization of acetate synthesis and suppression of methanogenesis by matching electron delivery with microbial uptake—an operational complement to hardware gains [4].

State of play (2024–2025 perspectives): Field overviews position CO_2-to-carboxylate MES around TRL 3 with throughputs approaching those in syngas/gas-fermentation trains in the best lab-scale plate/zero-gap systems, especially when integrated with downstream bioprocessing [43].

5.2. Techno-Economic Signals

Foundational TEAs indicate MES viability hinges on low carbon-intensity power and high areal current density (≈50–100 $mA \cdot cm^{-2}$), with stack voltage and CE as dominant levers; these targets have guided reactor/material design since 2020 [44]. Recent plate and zero-gap demonstrations report lower ohmic losses and better H_2 utilization, which directly reduce specific energy consumption and capex per m^2 of electrode—improving modeled cost per kg product [33,36]. Long-term operation with non-precious HER catalysts in zero-gap cells suggests a path to durable performance without noble metals, improving capex/opex assumptions and de-risking supply chains [46]. TEAs for electro-microbial production (EMP)—though not MES-only—show that coupling DAC/CO_2 capture + electrobiology can approach competitiveness for energy-dense fuels (e.g., n-butanol), if renewable power is cheap and conversion steps are intensified; the same cost drivers (electricity price, current density, productivity) map onto MES [10]. Reviews and perspectives [31,43] emphasize movement toward modular stacks and process intensification (gas-diffusion layers, integrated separations) as prerequisites for bankable pilots; key risks remain flooding/biofouling, H_2 slip, and operational durability beyond 1,000 h.

6. Conclusions

- Microbial electrosynthesis (MES) has progressed remarkably since its inception, moving from proof-of-concept studies in H-type reactors toward increasingly sophisticated systems that integrate novel electrode materials, microbial community engineering, and process optimization. The literature consistently highlights that electrode design and material innovation—ranging from carbonaceous substrates and graphene-based coatings to composite cathodes and biometallic oxides—are central drivers of improved performance, as they directly impact electron transfer efficiency, biofilm formation, and hydrogen evolution dynamics.
- Parallel to these advances, microbial community engineering has transitioned from reliance on mixed consortia to more controlled and, in some cases, genetically optimized strains, offering opportunities to fine-tune product selectivity and stability. Similarly, reactor configurations have evolved from simple two-chamber setups to plate, tubular, and zero-gap flow designs, significantly reducing ohmic losses and improving mass transfer.
- Despite these advances, several challenges remain. MES still faces critical barriers to scale-up, including insufficient long-term stability, hydrogen management inefficiencies, incomplete understanding of microbe–electrode interactions, and economic constraints tied to electricity demand and reactor capital costs. Current techno-economic assessments emphasize the need for higher current densities, improved Faradaic efficiencies, and durable low-cost materials to render MES competitive with conventional biotechnologies and power-to-X alternatives.
- Looking forward, the field is poised to benefit from integrative approaches—combining advanced material science, systems biology, and process engineering with data-driven modeling and techno-economic analysis. In particular, hybrid electrode architectures (graphene–oxide composites, catalytic coatings), biofilm engineering strategies, and intensified flow-through reactor designs hold promise for achieving the productivity thresholds required for industrial relevance. Furthermore, the alignment of MES research with renewable electricity integration and CO_2 circular economy initiatives underscores its potential role in decarbonization strategies.
- In conclusion, while MES is not yet a mature industrial technology, the trajectory of scientific progress between 2010 and 2025 signals a growing momentum toward practical application. Success will depend on bridging laboratory innovations with scalable, robust, and economically viable process configurations.

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References

1. K.P. Nevin, T.L. Woodward, A.E. Franks, Z.M. Summers, D.R. Lovley "Microbial Electrosynthesis: Feeding Microbes Electricity To Convert Carbon Dioxide and Water to Multicarbon Extracellular Organic Compounds", ASM Journals, 2010, vol. 1, no. 2, DOI: https://doi.org/10.1128/mbio.00103-10
2. L. Jourdin, T. Grieger, J. Monetti, V. Flexer, S. Freguia, Y. Lu, J. Chen, M. Romano, G.G. Wallace, J. Keller "High Acetic Acid Production Rate Obtained by Microbial Electrosynthesis from Carbon Dioxide", Environ. Sci. Technol. 2015, 49, 22, 13566–13574, DOI: https://doi.org/10.1021/acs.est.5b03821
3. I. Ibrahim, M. Slaehmin, K. Balachandran, M. Hil Me, K. Loh, M. Bakar, B. Jong, S. Lim "Role of microbial electrosynthesis system in CO_2 capture and conversion: a recent advancement toward cathode development", Front. Microbiol., 2023, Vol. 14, DOI: https://doi.org/10.3389/fmicb.2023.1192187
4. C. Zang, Q. Cao, J. Zhang, B. Fu, Y. Zhang, J. Zhang, F. Liu „Regulatory Mechanisms of Electron Supply Modes for Acetate Production in Microbial Electrosynthesis System", ACS Sustainable Chem. Eng. 2025, 13, 11, 4406–4417, DOI: https://doi.org/10.1021/acssuschemeng.4c08968
5. F. Harnish, J.S. Deutzmann, S.T. Boto, M.A. Rosenbaum "Microbial electrosynthesis: opportunities for microbial pure cultures", Trends in Biotechnology, 2024, vol. 42, issue 8, pp: 1035-1047, DOI: 10.1016/j.tibtech.2024.02.004
6. D. Zhang, J.L. Foo, M.W. Chang "Microbial electrosynthesis meets synthetic biology: Bioproduction from waste feedstocks", Biotechnology Notes, vol. 6, 2025, pp: 157-163, DOI: https://doi.org/10.1016/j.biotno.2025.05.001
7. G.S. Lekshmi, K. Bazaka, S. Ramakrishna, V. Kumaravel "Microbial electrosynthesis: carbonaceous electrode materials for CO2 conversion", Materials Horizons, 2023, vol 10, pp: 292-312, DOI: https://doi.org/10.1039/D2MH01178F
8. A. Al-Mamun, W. Ahmed, T. Jafary, J.K. Nayak, A. Al-Nuaimi, A. Sana "Recent advances in microbial electrosynthesis system: Metabolic investigation and process optimization", Biomedical Engineering Journal, 2023, Vol. 196, DOI: https://doi.org/10.1016/j.bej.2023.108928
9. S. Mills, P. Dessi, D. Pant, P. Ferras, W.T. Sloan, G. Collins, U. Z. Ijaz "A meta-analysis of acetogenic and methanogenic microbiomes in microbial electrosynthesis", Biofilms and microbiomes, 2022, Vol. 8, 73, DOI: https://doi.org/10.1038/s41522-022-00337-5
10. J.D. Adams, D. S. Clark "Techno-Economic Assessment of Electromicrobial Production of n-Butanol from Air-Captured CO2", Environ. Sci. Technol. 2024, 58, 17, 7302–7313, DOI: https://doi.org/10.1021/acs.est.3c08748
11. Y. H. Chu, Y.R. Lee, H.S. Kim, J. Lee, M. Moon, G.W. Park, S. Lee, S.Y. Lee "Evaluation of economic feasibility for the microbial electrosynthesis-based β-farnesene production technology: Process modeling and techno-economic assessment", Journal of CO2 utilization, 2025, vol. 97, DOI: https://doi.org/10.1016/j.jcou.2025.103110
12. L. Jourdin, S. Freguia, V. Flexer "Bringing High-Rate, CO2-Based Microbial Electrosynthesis Closer to Practical Implementation through Improved Electrode Design and Operating Conditions", Environ. Science and Technology, 2016, vol. 50, DOI:10.1021/acs.est.5b04431
13. Xu, M., Cobo, M.FA., Zeng, D. „Leveraging 3D printing in microbial electrochemistry research: current progress and future opportunities" Front. Environ. Sci. Eng. **19**, 1 (2025). https://doi.org/10.1007/s11783-025-1921-y
14. H. Liu, Y. Zeng, W. Chen, C. Liu „Effect of different hydrogen evolution rates at cathode on bioelectrochemical reduction of CO2 to acetate", The Science of The Total Environment, 2024, vol. 913, DOI:10.1016/j.scitotenv.2023.169744
15. R. Lin, X. Zheng, H. Zhang, H. Zhang, Y. He, M. Liu, L. Xie „Cathode catalyst-assisted microbial electrosynthesis of acetate from carbon dioxide: promising material selection", Journal of Environmental Sciences, 2025, DOI: https://doi.org/10.1016/j.jes.2025.04.038
16. J. Du, H. Liang, Y. Zou, B. Li, X. Li, L. Lin „Boosting Microbial CO2 Electroreduction by the Biocompatible and Electroactive Bimetallic Fe-Mn Oxide Cathode for Acetate Production", ACS Sustainable Chemistry & Engineering, 2024, vol. 12, issue 42, pp: 15659-15670, DOI: https://doi.org/10.1021/acssuschemeng.4c06214

17. T.H. Chung, A. Rahman, A.A. Chakrabarty, B.S. Zakaria, M. Khondoker, B. Dhar "3D printed cathodes for microbial electrolysis cell-assisted anaerobic digester: Evaluation of performance, resilience, and fluid dynamics", Journal of power sources, 2024, vol. 623, DOI: https://doi.org/10.1016/j.jpowsour.2024.235461
18. N. Chu, D. Wang, H. Wang, Q. Liang, J. Chang, Y. Gao, Y. Jiang, R. J. Zeng "Flow-Electrode Microbial Electrosynthesis for Increasing Production Rates and Lowering Energy Consumption" Engineering, 2023, vol. 25, issue 6, pp: 157-167, DOI: 10.1016/j.eng.2021.09.015
19. R. Gharbi, A. Gomez Vidales, S. Omanovic, B. Tartakovsky „Mathematical model of a microbial electrosynthesis cell for the conversion of carbon dioxide into methane and acetate", Journal of CO2 utilization, 2022, vol. 59, DOI: https://doi.org/10.1016/j.jcou.2022.101956
20. C. Marshall, D. Ross, E. Fichot, R. Norman, H. May "Long-term Operation of Microbial Electrosynthesis Systems Improves Acetate Production by Autotrophic Microbiomes", Environ. Sci. Technol. 2013, 47, 11, 6023–6029, DOI: https://doi.org/10.1021/es400341b
21. J. Hengsbach, B. Sabel-Becker, R. Ulber, D. Holtmann "Microbial electrosynthesis of methane and acetate—comparison of pure and mixed cultures", Appl Microbiol Biotechnol, 2022, vol. 106(12), pp:4427–4443. DOI: 10.1007/s00253-022-12031-9
22. L. F. Chen, H. Yu, J. Zhang, H. Y. Qin "A short review of graphene in the microbial electrosynthesis of biochemicals from carbon dioxide", RSC Adv., 2022, vol. 12, pp: 22770-22782, DOI: 10.1039/D2RA02038F
23. Q. Cao, C. Zhang, J. Zhang, J. Zhang, Z. Zheng, H. Liu "Enhanced microbial electrosynthesis performance with 3-D algal electrodes under high CO2 sparging: Superior biofilm stability and biocathode-plankton interactions", Bioresource Technology, 2024, vol. 412, DOI: https://doi.org/10.1016/j.biortech.2024.131381
24. F. Kracke, J. Deutzmann, B. Jayathilake, S. Pang, S. Chandrasekaran, S. Baker, A. Spormann "Efficient Hydrogen Delivery for Microbial Electrosynthesis via 3D-Printed Cathodes", Front. Microbiol., 2021, vol. 12, DOI: https://doi.org/10.3389/fmicb.2021.696473
25. E. Nwanebu, S. Omanovic, S. Hrapovic, A. Gomez Vidales, B. Tartakovsky "Carbon dioxide conversion to acetate and methane in a microbial electrosynthesis cell employing an electrically-conductive polymer cathode modified by nickel-based coatings", International Journal of Hydrogen Energy, 2022, vol. 47, pp: 203215, DOI: https://doi.org/10.1016/j.ijhydene.2021.10.003
26. R. Lin, X. Zheng, H. Zhang, Y. He, M. Liu, Li Xie „Cathode catalyst-assisted microbial electrosynthesis of acetate from carbon dioxide: promising material selection", Journal of Environmental Sciences, 2025, DOI: https://doi.org/10.1016/j.jes.2025.04.038
27. S. Tian, J. He, H. Huang, T.-S. Song, X. Wu, J. Xie, W. Zhou „Perovskite-Based Multifunctional Cathode with Simultaneous Supplementation of Substrates and Electrons for Enhanced Microbial Electrosynthesis of Organics", ACS Appl. Mater. Interfaces 2020, 12, 27, 30449–30456, DOI: https://doi.org/10.1021/acsami.0c07910
28. P. Izadi, J.-M. Fontmorin, A. Godain, E. H. Yu, I. M. Head „Parameters influencing the development of highly conductive and efficient biofilm during microbial electrosynthesis: the importance of applied potential and inorganic carbon source", NPJ Biofilms Microbiomes, 2020, vol. 6, issue 40, DOI: 10.1038/s41522-020-00151-x
29. D. Carrillo-Peña, R. Mateos, A. Morán, A. Escapa „Reduced graphene oxide improves the performance of a methanogenic biocathode", Fuel, 2022, vol. 321, DOI: https://doi.org/10.1016/j.fuel.2022.123957
30. S. Hui, Y. Jiang, Y. Jiang, Z. Lyu, S. Ding, B. Song, W. Zhu, J.-J. Zhu "Cathode materials in microbial electrosynthesis systems for carbon dioxide reduction: recent progress and perspectives", Energy Mater 2023; vol. 3, DOI: 10.20517/energymater.2023.60
31. H. Zhuab, Z. Dongab, Q. Huangc, T-S Song, J. Xie "Fe3O4/granular activated carbon as an efficient three-dimensional electrode to enhance the microbial electrosynthesis of acetate from CO2", *RSC Adv.*, 2019, vol. **9**, pp: 34095-34101, DOI: 10.1039/C9RA06255F
32. X.Ning,L. Liu, R.n Lin, R. O'Shea, C. Deng, X. Xuan, R. Xia, D. M. Wall, J. D. Murphy „Microbe-electrode interactions on biocathodes are facilitated through tip-enhanced electric fields during CO2-fed microbial electrosynthesis", Cell Reports Physical Science, 2024, vol. 5, DOI: https://doi.org/10.1016/j.xcrp.2024.102262.

33. B. Bian, N. Yu, N. Yun, S. Li, X. Zhou, C. Xie, R. Rossi, B. E. Logan “Substantially Improved Microbial Electrosynthesis of Methane Achieved by Improving Hydrogen Retention and Flow Distribution through Porous Electrodes”, Environ. Sci. Technol. 2025, vol. 59, issue 27, pp: 13719–13729, DOI: https://doi.org/10.1021/acs.est.5c02329
34. C. G. S. Giddings, K. P. Nevin, T. Woodward, D. R. Lovley, C. S. Butler „Simplifying microbial electrosynthesis reactor design”, Front Microbiol., 2015, vol 6, issue 468, DOI: 10.3389/fmicb.2015.00468
35. Z. Liu, X. Xue, W. Cai, K. Cui, S. A. Patil, K. Guo „Recent progress on microbial electrosynthesis reactor designs and strategies to enhance the reactor performance”, Biochemical Engineering Journal, 2023, vol. 190, DOI: https://doi.org/10.1016/j.bej.2022.108745
36. J. S. Deutzmann, G. Callander, A.M. Spormann „Improved reactor design enables productivity of microbial electrosynthesis on par with classical biotechnology”, Bioresource Technology, 2025, vol. 416, DOI: https://doi.org/10.1016/j.biortech.2024.131733
37. S. Bajracharya, A. Krige, L. Matsakas, U. Rova, P. Christakopoulos „Advances in cathode designs and reactor configurations of microbial electrosynthesis systems to facilitate gas electro-fermentation”, Bioresource Technology, 2022, vol. 354, DOI: https://doi.org/10.1016/j.biortech.2022.127178
38. M. Stöckl, T. Lange, P. Izadi, S. Bolat, N. Teetz, F. Harnisch, D. Holtmann „Application of gas diffusion electrodes in bioeconomy: An update”, Biotechnology and bioengineering, 2023, DOI: https://doi.org/10.1002/bit.28383
39. D.A Corona-Martínez, S. Y Martínez-Amador, J.A Rodríguez-De la Garza, E. I Laredo-Alcalá, P. Pérez-Rodríguez „Recent Advances in Scaling up Bioelectrochemical Systems: A Review”, BioTech (Basel), 2025, vol. 14(1), DOI: 10.3390/biotech14010008
40. A. Fathima, I.M.S.K. Ilankoon, Y. Zhang, M. N. Chong „Scaling up of dual-chamber microbial electrochemical systems – An appraisal using systems design approach”, Science of The Total Environment, 2024, vol. 912, DOI: https://doi.org/10.1016/j.scitotenv.2023.169186
41. E. Nwanebua, M. Jezernikb, C. Lawsonb, G. Bruanta, B. Tartakovsky “Impact of cathodic pH and bioaugmentation on acetate and CH4 production in a microbial electrosynthesis cell”, RSC Adv., 2024, vol 14, pp: 22962-22973, DOI: 10.1039/D4RA03906H
42. N. Rohbohm, L. T Angenent „A development study for liquid- and vapor-fed anode zero-gap bioelectrolysis cells”, iScience, 2025, vol. 28(7), DOI: 10.1016/j.isci.2025.112959
43. O. Cabau-Peinado, M. Winkelhorst, R. Stroek, R. de Kat Angelino, A. K. Masania, J.M. Daran[1] · L. Jourdin „Microbial electrosynthesis from CO2 reaches productivity of syngas and chain elongation fermentations”, Trends in Biotechnology, 2024, vol. 42, issue 11, pp: 1503-1522, DOI: DOI: 10.1016/j.tibtech.2024.06.005
44. L. Jourdin, J. Sousa, N. van Stralen, D. Strik „Techno-economic assessment of microbial electrosynthesis from CO2 and/or organics: An interdisciplinary roadmap towards future research and application”, Applied Energy, 2020, vol. 279, DOI: https://doi.org/10.1016/j.apenergy.2020.115775
45. Y. Bian, A. Leininger, H. D May, Z. J. Ren „H2 mediated mixed culture microbial electrosynthesis for high titer acetate production from CO2”, Environ Sci Ecotechnol, 2023; vol. 19:100324. DOI: 10.1016/j.ese.2023.100324
46. B. Bian, N. Yu, A. Akbari, L. Shi, X. Zhou, C. Xie, P. E. Saikaly, B. E. Logan „Using a non-precious metal catalyst for long-term enhancement of methane production in a zero-gap microbial electrosynthesis cell”, Water Research, 2024, vol. 259, DOI: https://doi.org/10.1016/j.watres.2024.121815