

Electrifying the Biorefinery: Engineering Challenges and Molecular Insights into Semi-Synthetic Electromicrobial Processes

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Abstract—Semi-synthetic electromicrobial systems represent a transformative approach to CO₂ valorization, coupling electrochemical reduction with microbial biosynthesis to produce fuels, chemicals, and materials from renewable electricity and waste carbon. These hybrid platforms transcend the efficiency limits of natural photosynthesis by integrating fast, selective electrocatalysis with the metabolic versatility of engineered microorganisms. Recent advances demonstrate that C2 intermediate relay strategies—where electrochemically generated ethanol or acetate feeds microbial fermentation—achieve 6–8× higher biomass productivity than C1 or H₂-mediated routes (Zhang et al., 2022). Flow electrolyzers with gas diffusion electrodes now operate at industrially relevant current densities (100–200 mA cm⁻²) with ~15% Faradaic efficiency for soluble C2 products in biocompatible electrolytes (Zhang et al., 2022). However, significant challenges remain: electron transfer bottlenecks at bio-abiotic interfaces, oxygen toxicity from conventional anodes, biofilm community instability, and insufficient techno-economic validation. This review synthesizes mechanisms of CO₂ reduction, interface engineering strategies, conductive scaffold materials, reactor design principles, and pathways toward industrial decarbonization, identifying critical research directions for realizing scalable electromicrobial biorefineries.

Index Terms—electromicrobial systems, biosynthesis, electrocatalysis, microbial fermentation, biocompatible, industrial decarbonation.

I. INTRODUCTION

Semi-Synthetic Electromicrobial Systems for CO₂ Valorization

The urgent need to mitigate anthropogenic CO₂ emissions while transitioning to sustainable chemical manufacturing has catalyzed the development of semi-synthetic electromicrobial systems—hybrid platforms that integrate electrochemical CO₂ reduction with microbial biosynthesis (Tan & Nielsen, 2022; Zhang et al., 2022). These systems exploit the complementary strengths of abiotic electrocatalysis (fast kinetics, tunable selectivity) and biological conversion (high product specificity, metabolic diversity) to transform CO₂ and renewable electricity into value-added chemicals, fuels, and materials (Tan & Nielsen, 2022; Zhang et al., 2023). Unlike purely electrochemical or biological approaches, electromicrobial hybrids can overcome fundamental limitations of each domain: electrochemistry struggles with C–C coupling for complex molecules, while biology faces slow electron uptake and limited energy efficiency (Lai et al., 2023; Rowe et al., 2021; Weliwatte & Minteer, 2021).

The Pivot Toward Decarbonization

Industrial chemical production currently relies on fossil carbon feedstocks, contributing approximately 10% of global CO₂ emissions (M. & A., 2024). Electromicrobial biorefineries offer a pathway to circular carbon economies by capturing CO₂ from point sources or the atmosphere and converting it into drop-in fuels, platform chemicals, and biopolymers using renewable electricity (Abel et al., 2022; Chandrasekhar et al., 2021; Mustafa et al., 2025). This electrification of biosynthesis decouples chemical manufacturing from fossil resources and enables modular, distributed production that can be co-located with renewable energy generation or

industrial CO₂ sources (Chandrasekhar et al., 2021; Zhang et al., 2022). Recent techno-economic analyses suggest that electromicrobial routes could become competitive with conventional petrochemical processes as renewable electricity costs decline and carbon pricing mechanisms mature (Abel et al., 2022; Sheppard et al., 2022).

Fusion of Electrochemistry and Synthetic Biology

The convergence of electrochemistry and synthetic biology has enabled unprecedented control over electron flow and metabolic pathways in electromicrobial systems (Guo et al., 2024; Lai et al., 2023; Zhang et al., 2023). Electrochemical CO₂ reduction generates C1 intermediates or C2 products (ethanol, acetate) that serve as electron and carbon sources for engineered microbes (Boto et al., 2023; Tan & Nielsen, 2022; Zhang et al., 2022). Synthetic biology tools—including CRISPR-based genome editing, heterologous expression of electron transfer proteins, and metabolic pathway optimization—allow researchers to tailor microbial chassis for efficient uptake of electrochemical products and channeling of carbon flux toward target molecules (Lai et al., 2023; Mustafa et al., 2025; Zhang et al., 2023). This bio-abiotic integration creates modular "plug-and-play" systems where electrochemical and biological modules can be independently optimized and reconfigured for different products (Bakonyi et al., 2022; Boto et al., 2023; Liu et al., 2022).

Transcending Natural Photosynthesis

Natural photosynthesis converts solar energy to biomass with theoretical maximum efficiencies of ~11% but typically achieves <1% in practice due to light saturation, photorespiration, and metabolic constraints (Mirea et al., 2025; Weliwatte & Minteer, 2021). Electromicrobial systems bypass these limitations by directly supplying electrons at controlled potentials, eliminating light-harvesting inefficiencies and enabling operation at higher volumetric productivities (Mirea et al., 2025; Rohbohm et al., 2024). Hybrid photo-bioelectrocatalytic systems that combine light-driven water splitting with microbial CO₂ fixation have demonstrated solar-to-chemical efficiencies exceeding 10%, surpassing natural photosynthesis (Weliwatte & Minteer, 2021). Moreover, electromicrobial platforms operate continuously regardless of diurnal cycles and can be scaled vertically in compact bioreactors, offering land-use

advantages over crop-based biofuel production (Mirea et al., 2025; Sheppard et al., 2022).

II. MECHANISMS OF CO₂ VALORIZATION

Electron Transfer Pathways

Electromicrobial CO₂ valorization proceeds through three primary electron transfer mechanisms: (a) direct electron uptake from cathodes, (b) H₂-mediated electron transfer, and (c) chemical intermediate relay via C1 or C2 compounds (Boto et al., 2023; J. Zhang et al., 2023; P. Zhang et al., 2022). Each pathway exhibits distinct mass-transfer characteristics, energetic efficiencies, and compatibility with different microbial chassis.

Direct electron uptake involves microbial cells accepting electrons directly from cathode surfaces through extracellular electron transfer proteins, conductive pili, or biofilm matrices (Song et al., 2021; Xue et al., 2024). While this mechanism minimizes intermediate losses, it suffers from low electron flux per cell and requires intimate electrode-microbe contact, limiting volumetric productivity (Guo et al., 2024; Liu et al., 2022). Recent work has identified inward EET pathways in *Shewanella oneidensis* involving multiheme c-type cytochromes and quinone pools, though electron uptake rates remain orders of magnitude lower than outward EET for electricity generation (Rowe et al., 2021; Zhang et al., 2023).

H₂-mediated electron transfer uses electrochemically generated hydrogen as a soluble electron carrier that microbes oxidize via hydrogenases to drive CO₂ fixation through pathways like the Wood-Ljungdahl pathway (Boto et al., 2023; Kracke et al., 2021). This approach decouples electrode surface area from microbial growth but faces gas-liquid mass transfer limitations and H₂ escape losses (Zhu et al., 2022). Optimized 3D-printed cathode geometries with high surface areas have achieved volumetric methane productivities of 2.2 L CH₄ L⁻¹ day⁻¹ with ~99% coulombic efficiency by improving in situ H₂ delivery and reducing bubble formation (Kracke et al., 2021).

C1/C2 intermediate relay strategies employ electrochemical CO₂ reduction to generate soluble intermediates—CO, formate (C1) or ethanol, acetate (C2)—that microbes metabolize aerobically or anaerobically (Tan & Nielsen, 2022; J. Zhang et al.,

2023; P. Zhang et al., 2022). C1 carriers have lower energy content per carbon and can limit aerobic fermentation efficiency, while C2 intermediates support faster microbial growth and higher productivities (Zhang et al., 2022). Integrated electro-microbial conversion systems using C2 relay demonstrated $\sim 6\times$ and $\sim 8\times$ higher biomass productivity compared to C1 and H₂ routes, respectively (Zhang et al., 2022).

Faradaic Efficiencies and Performance Metrics

Electrochemical CO₂ reduction to C2 products on copper catalysts in flow cells with gas diffusion electrodes has achieved current densities of 100–200 mA cm⁻² with total Faradaic efficiencies for soluble C2 products around 15% in biocompatible phosphate electrolytes (Zhang et al., 2022). While lower than the >60% C2 Faradaic efficiencies reported in alkaline electrolytes, phosphate-buffered systems maintain pH stability and ionic strength compatible with downstream microbial cultivation (Zhang et al., 2022). Acetate selectivity in CO₂ electroreduction on copper is strongly influenced by local mass transport and pH, with 30–60% acetate selectivity observed under specific conditions (Pan, 2025).

For microbial electrosynthesis systems, acetate production rates range from 5.1 ± 0.2 mmol L⁻¹ day⁻¹ in baseline systems to 7.4 ± 0.4 mmol L⁻¹ day⁻¹ with artificial mediators, achieving volumetric titers of 8.1–13.3 g L⁻¹ and coulombic efficiencies of 87–92% (Song et al., 2021). Current densities in MES reactors typically range from 3.4 to 14.5 A m⁻², substantially lower than electrochemical systems but sufficient for continuous operation (Song et al., 2021). Methane production via electromethanogenesis has achieved coulombic efficiencies exceeding 90% in optimized systems (Horváth-Gönczi et al., 2023; Rohbohm et al., 2024).

EMC2 Systems and Quantitative Performance

Electro-microbial conversion systems integrate electrochemical CO₂ reduction with microbial fermentation in tandem or single-pot configurations (Cui et al., 2025; Zhang et al., 2022). In a representative EMC2 system for bioplastic production, electrochemical generation of C2 intermediates (ethanol, acetate) at 100–200 mA cm⁻² with $\sim 15\%$ Faradaic efficiency supplied sufficient carbon flux to support rapid microbial growth and polyhydroxyalkanoate accumulation (Zhang et al., 2022). The C2 relay strategy enabled aerobic

fermentation with higher ATP yields compared to anaerobic acetogenesis, accelerating biomass accumulation and product synthesis (Zhang et al., 2022).

Comparative studies demonstrate that C2 intermediates outperform C1 and H₂ routes across multiple metrics. Formate and methanol present kinetic and energetic integration challenges with cellular cofactors, while H₂ routes are constrained by gas-liquid transfer and hydrogenase kinetics (Boto et al., 2023; Zhang et al., 2022). The superior performance of C2 relay systems stems from higher energy content per carbon, compatibility with aerobic metabolism, and elimination of gas-phase mass transfer limitations (Zhang et al., 2022).

III. BIO-ABIOTIC INTERFACE ENGINEERING

Extracellular Electron Transfer Mechanisms

The bio-abiotic interface—where electrons transfer from electrodes to microbial cells—represents a critical bottleneck in electromicrobial systems (Guo et al., 2024; Liu et al., 2022). Inward extracellular electron transfer relies on multiheme c-type cytochromes, conductive appendages (pili or nanowires), and redox-active biofilm matrices (Rowe et al., 2021; Song et al., 2021; Zhang et al., 2023). In *Shewanella oneidensis*, the Mtr pathway comprising outer membrane cytochromes MtrC, MtrA, and MtrB facilitates bidirectional electron transfer, though inward flux rates remain 10–100 $\times$ lower than outward transfer (Rowe et al., 2021; Zhang et al., 2023). Recent identification of electron uptake pathways in *Shewanella* revealed quinone-mediated electron entry coupled to menaquinone pools, providing molecular targets for engineering enhanced electron uptake (Rowe et al., 2021).

Biofilm matrices composed of extracellular polymeric substances, proteins, and conductive minerals can facilitate electron transfer between planktonic cells and electrodes (Song et al., 2021; Zhang et al., 2023). Biofilm-driven microbial electrosynthesis models indicate that biofilm thickness, porosity, and conductivity significantly influence current density and product formation rates (Cabau-Peinado et al., 2021). Tip-enhanced electric fields at electrode surface features have been shown to facilitate microbe-electrode interactions during

CO₂-fed MES, suggesting that electrode topography influences EET efficiency (Xue et al., 2024).

Multiheme c-Type Cytochromes and Protein Engineering

Multiheme c-type cytochromes serve as biological electron conduits, shuttling electrons across cell membranes through sequential redox reactions (Rowe et al., 2021; Zhang et al., 2023). Engineering strategies to enhance inward EET include: overexpression of native EET complexes heterologous expression of EET proteins in non-native hosts directed evolution to improve electron transfer kinetics, and optimization of cytochrome maturation pathways (Lai et al., 2023; Zhang et al., 2023). Expression of *Shewanella* Mtr proteins in *Escherichia coli* enabled electron uptake for CO₂ reduction, though rates remained suboptimal due to incomplete cytochrome maturation and membrane integration (Zhang et al., 2023).

Protein engineering of electron conduit proteins aims to lower interfacial overpotentials and increase electron flux (Guo et al., 2024). Rational design and directed evolution of cytochromes have improved midpoint potentials and electron transfer rates in some systems, but systematic engineering frameworks for inward EET remain underdeveloped compared to outward EET for microbial fuel cells (Lai et al., 2023; Zhang et al., 2023).

Mediator Systems: Neutral Red and HNQ

Artificial redox mediators—small molecules that shuttle electrons between electrodes and cells—offer an alternative to direct EET (Song et al., 2021; Xu et al., 2021). Neutral red and 2-hydroxy-1,4-naphthoquinone have demonstrated significant improvements in acetate synthesis by facilitating electron transport between suspended cells and electrodes (Song et al., 2021). In MES systems, addition of NR or HNQ increased acetate production rates from 5.1 to 7.4 mmol L⁻¹ day⁻¹, with volumetric titers reaching 13.3 g L⁻¹ and coulombic efficiencies of 92% (Song et al., 2021). These mediators bind to cell membranes and exchange electrons with intracellular enzymes and cofactors, bypassing the need for direct electrode contact (Song et al., 2021).

Tuning the redox potential of mediators through chemical modification can optimize electron transfer thermodynamics (Xu et al., 2021). Anthraquinone-2-sulfonate derivatives with tailored redox potentials have shown improved electron transfer kinetics in

Shewanella oneidensis, demonstrating the potential for rational mediator design (Xu et al., 2021). However, mediator stability, toxicity, and cost remain challenges for large-scale implementation (Song et al., 2021).

Surface Functionalization and Synthetic Biology Targets

Electrode surface functionalization with redox-active polymers, immobilized mediators, or biomolecules can enhance electron transfer and microbial attachment (Agee et al., 2023; Song et al., 2021). Conductive polymers based on poly-3-hexylthiophene (P3HT), including methylimidazolium-functionalized variants, exhibit both electronic and ionic conductivity and improve mediated electron transfer in *Shewanella oneidensis* (Agee et al., 2023). These polymers enhance current generation and show improved biocompatibility compared to bare electrodes (Agee et al., 2023).

Synthetic biology targets for interface engineering include: overexpression of c-type cytochromes and EET complexes engineering quinone and methanol dehydrogenase pathways for improved C1 handling rewiring central carbon fixation pathways (e.g., Calvin-Benson-Bassham, Wood-Ljungdahl, or synthetic glycine pathways) to enhance CO₂ assimilation, and coupling electron uptake to redox sinks that drive biosynthesis (Lai et al., 2023; Mustafa et al., 2025; Zhang et al., 2023). Integration of these strategies with electrode engineering promises to overcome current electron transfer bottlenecks (Guo et al., 2024; Liu et al., 2022).

IV. CONDUCTIVE SCAFFOLD MATERIALS

Carbon-Based Materials

Carbon-based electrode materials—including graphite, carbon felt, carbon cloth, carbon nanotubes, and graphene—dominate electromicrobial systems due to their high electrical conductivity, tunable porosity, chemical stability, and biocompatibility (Chen et al., 2022; Herkendell, 2021; Langsdorf et al., 2021). Graphene and reduced graphene oxide offer exceptional surface areas (>1000 m² g⁻¹) and conductivity, boosting bacterial loading and electron transfer rates (Chen et al., 2022). Composites such as RGO-tetraethylenepentamine, platinum nanoparticles on RGO (PtNPs/RGO), and MnO₂/RGO enhance

catalytic activity and surface functionality for improved MES performance (Chen et al., 2022).

Three-dimensional carbon aerogel cathodes fabricated by additive manufacturing enable custom geometries with high surface-area-to-volume ratios (Kracke et al., 2021; Liu et al., 2022). When plated with nickel-molybdenum alloy catalysts, 3D-printed carbon aerogel cathodes achieved sustained electromethanogenesis at $2.2 \text{ L CH}_4 \text{ L}^{-1} \text{ day}^{-1}$ with ~99% coulombic efficiency (Kracke et al., 2021). The 3D architecture improves in situ H_2 delivery, reduces bubble formation, and mitigates local pH gradients, addressing key mass transfer limitations (Kracke et al., 2021).

Carbonaceous matrices derived from biomass offer low-cost, sustainable electrode materials with naturally high surface areas, porous structures for mass transport, and good biocompatibility due to higher hydrophilicity compared to synthetic carbons (Langsdorf et al., 2021). However, biomass-derived carbons may exhibit higher internal resistance and require activation or functionalization to achieve optimal performance (Herkendell, 2021).

Nanostructured Metals and Metal Catalysts

Metal-based electrodes and catalysts—including platinum, nickel, titanium, stainless steel, copper, silver, and gold—provide enhanced conductivity and electrocatalytic activity for CO_2 reduction and H_2 evolution (Horváth-Gönczi et al., 2023; Kracke et al., 2021; Tan & Nielsen, 2022). Copper is unique among metals for its ability to catalyze C–C coupling, producing C_2^+ products like ethanol, acetate, and ethylene from CO_2 (Tan & Nielsen, 2022; Zhang et al., 2022). Sputtered copper films on gas diffusion layers of PTFE or carbon paper achieved industrially relevant current densities ($100\text{--}200 \text{ mA cm}^{-2}$) and ~15% Faradaic efficiency for soluble C_2 products in biocompatible phosphate electrolytes (Zhang et al., 2022).

Noble metal catalysts exhibit high activity for specific reactions—Au and Ag for CO production (>90% Faradaic efficiency), Pt for H_2 evolution—but face cost and scalability challenges (Pan, 2025; Tan & Nielsen, 2022). Bimetallic and alloy catalysts (e.g., NiMo, CuZn) offer tunable selectivity and improved stability compared to pure metals (Kracke et al., 2021). However, metal electrodes may suffer from biocompatibility issues, corrosion, and biofouling,

requiring surface treatments or coatings (Horváth-Gönczi et al., 2023).

Metal-Organic Frameworks

Metal-organic frameworks—crystalline porous materials composed of metal nodes and organic linkers—have emerged as promising electrode materials and catalyst supports due to their high porosity (up to 90% free volume), tunable pore sizes, and chemical versatility (Gupta et al., 2024; Mirea et al., 2025). MOFs can integrate catalytic sites for CO_2 reduction with high surface areas for microbial attachment, potentially serving as multifunctional bio-abiotic interfaces (Gupta et al., 2024). MXene-based electrodes (2D transition metal carbides/nitrides) functionalized with carbon nanotubes or MOFs have shown improved CO_2 conversion yields in microbial electrosynthesis, with MOF coatings providing cytoprotective layers against reactive radical species (Gupta et al., 2024).

Despite their promise, MOF applications in electromicrobial systems remain at the research scale, with challenges including electrical conductivity (most MOFs are insulators), stability in aqueous electrolytes, and scalable synthesis (Gupta et al., 2024; Mirea et al., 2025). Conductive MOFs incorporating redox-active linkers or metal nodes offer potential solutions but require further development (Mirea et al., 2025).

Conductive Polymers and Composites

Conductive polymers—such as polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene), and poly-3-hexylthiophene (P3HT)—facilitate enzyme immobilization, mediator incorporation, and microbial adhesion while providing tunable electrical and mechanical properties (Agee et al., 2023; Song et al., 2021). P3HT-based polymers with methylimidazolium functionalization exhibit both electronic and ionic conductivity, enhancing mediated electron transfer and biocompatibility in *Shewanella oneidensis* bioelectrochemical systems (Agee et al., 2023). These polymers reduce interfacial resistance and improve current generation compared to bare carbon electrodes (Agee et al., 2023).

Composite materials combining carbon supports with metal nanoparticles, conductive polymers, or MOFs leverage synergistic properties to optimize conductivity, catalytic activity, surface area, and biocompatibility (Chen et al., 2022; Gupta et al., 2024; Song et al., 2021). For example, copper ferrite

nanoparticles on RGO enhance both electrocatalytic CO₂ reduction and microbial attachment (Chen et al., 2022). However, composite fabrication complexity and cost must be balanced against performance gains for practical applications (Herkendell, 2021; Mirea et al., 2025).

Comparative Analysis and Scalability

Table 1 summarizes key properties, representative performance metrics, and trade-offs for major electrode material classes in electromicrobial systems.

Material Class	Key Properties	Representative Performance	Advantages	Limitations
Carbon-based	High conductivity, tunable porosity, good biocompatibility, high surface area	3D-printed carbon aerogel + NiMo: 2.2 L CH ₄ L ⁻¹ day ⁻¹ , ~99% CE (Kracke et al., 2021); Graphene: enhanced bacterial loading (Chen et al., 2022)	Low cost, chemical stability, scalable fabrication, excellent biofilm support	Variable internal resistance, may require functionalization
Nanostuctured metals	High catalytic activity, tunable selectivity, excellent conductivity	Sputtered Cu GDEs: 100–200 mA cm ⁻² , ~15% FE for C ₂	Superior electrocatalytic performance, precise control of	High cost (noble metals), corrosion, potential biocom

		products (Zhang et al., 2022); Au/Ag: >90% FE for CO (Tan & Nielsen, 2022)	product selectivity	patibility issues, limited scalability
Metal-organic frameworks	Ultra-high porosity, chemical tunability, integrated catalyst/supp	MXene-MOF composites: improved CO ₂ conversion yields (Gupta et al., 2024)	Multifunctional interfaces, tunable pore chemistry, high surface area	Low electrical conductivity, aqueous stability concerns, scalable synthesis is challenges
Conductive polymers	Tunable electrical/mechanical properties, mediator immobilization, enzyme compatibility	P3HT-Im ⁺ : enhanced electron transfer and biocompatibility (Agee et al., 2023)	Flexible design, reduced interfacial resistance, good biocompatibility	Moderate conductivity, long-term stability questions, synthesis is complexity

Scalability considerations favor carbon-based materials due to established manufacturing processes, low cost, and material availability (Herkendell, 2021; Liu et al., 2022). Modular carbon electrode assemblies have been proposed for scalable bioelectrochemical system architectures (Bakonyi et al., 2022; Herkendell, 2021). Metal catalysts, particularly copper for C₂ production, require cost-

effective deposition methods such as sputtering or electrodeposition onto carbon supports to balance performance and economics (Zhang et al., 2022). MOFs and conductive polymers remain promising but require advances in synthesis, stability, and integration before large-scale deployment (Gupta et al., 2024; Mirea et al., 2025).

V. REACTOR DESIGN PRINCIPLES

Flow Electrolyzers and GDE Configurations

Flow electrolyzers with gas diffusion electrodes represent the state-of-the-art for electrochemical CO₂ reduction, overcoming gas-liquid mass transfer limitations that constrain batch reactors (Liu et al., 2022; Zhang et al., 2022). GDE flow cells supply gaseous CO₂ directly to the catalyst layer through a porous, hydrophobic backing (typically PTFE or carbon paper), achieving current densities of 100–200 mA cm⁻² for C₂ production—orders of magnitude higher than aqueous-fed systems (Liu et al., 2022; Zhang et al., 2022). This configuration is essential for supplying sufficient carbon flux to downstream microbial conversion in EMC₂ systems (Cui et al., 2025; Zhang et al., 2022).

Zero-gap configurations, where the cathode and anode are separated only by a thin ion-exchange membrane or separator, minimize ohmic losses and enable compact reactor designs (Pang & Zhu, 2025). Three-dimensional printed electrodes with optimized flow channels and electrode geometries further enhance mass transfer and current distribution (Kracke et al., 2021; Zegers et al., 2025). However, GDE stability in aqueous electrolytes remains a challenge, with flooding and catalyst deactivation limiting operational lifetimes (Zhang et al., 2022).

Mass Transfer and H₂ Delivery

Mass transfer of gaseous substrates (CO₂, H₂) and products (H₂, CH₄) critically influences electromicrobial system performance (Cabau-Peinado et al., 2021; Kracke et al., 2021). For H₂-mediated systems, gas-liquid transfer limitations and H₂ escape losses reduce coulombic efficiency and productivity (Kracke et al., 2021). Optimized 3D-printed cathode geometries with high surface areas (up to 382.63 cm² L⁻¹ surface-area-to-reactor-volume ratio) improve in situ H₂ delivery by reducing local current densities, minimizing bubble formation, and decreasing H₂ escape (Kracke et al., 2021). These designs enabled

volumetric methane productivities of 2.2 L CH₄ L⁻¹ day⁻¹ with near-unity coulombic efficiencies (Kracke et al., 2021).

Continuous sparging of CO₂ at controlled flow rates (typically 0.1–1 L min⁻¹) maintains dissolved CO₂ concentrations and removes gaseous products, preventing product inhibition (Boto et al., 2023; Zhu et al., 2022). Stirring or recirculation enhances convective mass transfer, reducing concentration gradients and improving current distribution (Boto et al., 2023). However, excessive agitation can disrupt biofilms and increase energy consumption, requiring optimization for each system (Liu et al., 2022).

Biofilm Management and Community Control

Cathodic biofilm composition evolves over time and can allow re-emergence of undesired methanogens in acetogenic MES systems, compromising product selectivity (Mills et al., 2022). A meta-analysis of acetogenic and methanogenic microbiomes in MES revealed an 80% shared cathodic core microbiome across systems, with inoculum pretreatments strongly affecting community trajectories (Mills et al., 2022). This finding implies that active community management—through selective enrichment, antimicrobial agents, or operational parameter control (pH, potential, substrate availability)—is required for stable product selectivity (Abdollahi et al., 2022; Mills et al., 2022).

Biofilm thickness and architecture influence electron transfer efficiency and mass transport (Cabau-Peinado et al., 2021). Thin, conductive biofilms maximize electron flux per unit electrode area, while thick biofilms may suffer from diffusion limitations and dead zones (Cabau-Peinado et al., 2021; Song et al., 2021). Periodic biofilm harvesting or controlled detachment can maintain optimal biofilm thickness and prevent reactor clogging (Liu et al., 2022). Spatial arrangement of cathodes and reactor geometry also affect microorganism-electrode interactions and biofilm development (Chen et al., 2022; Zegers et al., 2025).

Anode Oxygen Dilemma

The conventional oxygen evolution reaction at the anode creates an engineering dilemma for electromicrobial systems because oxygen is toxic to many cathodic electrotrophs, particularly strict anaerobes like acetogens and methanogens (Abdollahi et al., 2022). Oxygen penetration to the cathode chamber—through membrane crossover,

leaks, or incomplete separation—poisons anaerobic metabolism and reduces coulombic efficiency (Abdollahi et al., 2022; Rohbohm et al., 2024). Strategies to address the oxygen dilemma include: physical separation with gas-tight membranes and purging oxygen-scavenging chemicals or enzymes alternative anodic oxidations (e.g., organic waste oxidation, sulfide oxidation), and use of facultative or aerotolerant microbes (Abdollahi et al., 2022; Chandrasekhar et al., 2021; Rohbohm et al., 2024). Alternative anode reactions that avoid oxygen generation offer potential solutions but introduce complexity and may reduce overall system efficiency (Abdollahi et al., 2022). For example, coupling MES cathodes with microbial fuel cell anodes that oxidize organic waste can eliminate oxygen production while treating wastewater, creating integrated bioelectrochemical systems (Chandrasekhar et al., 2021; Horváth-Gönczi et al., 2023). However, such configurations require careful matching of anode and cathode kinetics and potentials (Abdollahi et al., 2022).

Continuous Operation and Modular Manufacturing
Continuous-flow operation with steady-state substrate supply and product removal enables higher volumetric productivities and easier process control compared to batch systems (Cabau-Peinado et al., 2021; Liu et al., 2022). Continuous MES reactors with chemostat-mode operation have demonstrated stable acetate production over extended periods (weeks to months) with consistent coulombic efficiencies (Rohbohm et al., 2024; Song et al., 2021). Membrane-less configurations that eliminate ion-exchange membranes reduce cost and complexity while maintaining product separation through pH gradients or selective product recovery (Mirea et al., 2025).

Modular reactor designs—where electrochemical and biological modules are staged in cascades or integrated in single vessels—offer flexibility for different products and operating conditions (Bakonyi et al., 2022; Zegers et al., 2025). Staging allows independent optimization of electrochemical CO₂ reduction (high current density, low pH) and microbial fermentation (moderate current density, neutral pH, aerobic or anaerobic) (Tan & Nielsen, 2022; Zhang et al., 2022). Modular manufacturing approaches, including 3D printing and standardized electrode assemblies, facilitate scale-up and

customization for specific applications (Kracke et al., 2021; Park et al., 2025; Zegers et al., 2025).

VI. TOWARD INDUSTRIAL DECARBONIZATION

Techno-Economic Considerations

Techno-economic analyses of electromicrobial systems identify electrode cost, system integration complexity, and low volumetric productivity as primary barriers to commercial competitiveness (Abel et al., 2022; Herkendell, 2021; Sheppard et al., 2022). Electrode materials account for 20–40% of capital costs in bioelectrochemical systems, with precious metal catalysts and ion-exchange membranes contributing significantly (Herkendell, 2021). Replacing noble metals with earth-abundant catalysts and developing membrane-less configurations are critical cost-reduction strategies (Abdollahi et al., 2022; Mirea et al., 2025; Zhang et al., 2022).

Volumetric productivity—the rate of product formation per unit reactor volume—directly impacts capital costs and footprint (Park et al., 2025; Singh et al., 2023). Current MES systems achieve acetate productivities of 5–15 mmol L⁻¹ day⁻¹ (0.3–0.9 g L⁻¹ day⁻¹), substantially lower than conventional fermentation (>10 g L⁻¹ day⁻¹) (Liu et al., 2022; Song et al., 2021). Increasing current densities, improving electron transfer rates, and optimizing reactor configurations are essential to close this productivity gap (Liu et al., 2022; Park et al., 2025). Upper limit efficiency estimates for electromicrobial production of drop-in jet fuels suggest theoretical feasibility but highlight the need for substantial performance improvements (Sheppard et al., 2022).

Energy efficiency—the fraction of electrical energy converted to chemical energy in products—determines operating costs and environmental benefits (Abel et al., 2022; Bakonyi et al., 2022). Electromicrobial systems typically operate at 20–60% energy efficiency, with losses from overpotentials, side reactions, and metabolic inefficiencies (Bakonyi et al., 2022; Liu et al., 2022). Minimizing overpotentials through catalyst and interface engineering, maximizing Faradaic efficiency, and coupling to low-cost renewable electricity are key strategies for improving energy

economics (Liu et al., 2022; Pan, 2025; Zhang et al., 2022).

Life Cycle Assessment Perspectives

Life cycle assessment evaluates the environmental impacts of electromicrobial systems across their entire lifecycle, from material extraction to end-of-life disposal (Abel et al., 2022; Bakonyi et al., 2022). A comparative LCA of electromicrobial production systems found that electricity source dominates environmental footprint, with renewable electricity (wind, solar) providing substantial greenhouse gas reductions compared to grid electricity (Abel et al., 2022). However, electrode material production, particularly for metal catalysts and carbon nanostructures, contributes significantly to embodied energy and emissions (Abel et al., 2022; Singh et al., 2023).

Product recovery and purification—often energy-intensive processes involving distillation, extraction, or chromatography—can offset environmental benefits if not optimized (Bakonyi et al., 2022; Singh et al., 2023). Integrated product separation strategies, such as in situ extraction with biocompatible solvents or membrane-based recovery, reduce downstream processing burdens (Chandrasekhar et al., 2021; Singh et al., 2023). Circular economy approaches that recycle electrode materials and utilize waste CO₂ and electricity further improve LCA metrics (Chandrasekhar et al., 2021; Langsdorf et al., 2021).

Circular Carbon Strategies

Electromicrobial biorefineries enable circular carbon strategies by converting CO₂ from industrial point sources (cement, steel, chemical plants) or direct air capture into chemicals and fuels that can be used, combusted, and recaptured (Abel et al., 2022; Chandrasekhar et al., 2021; M. & A., 2024). This carbon cycling reduces net CO₂ emissions compared to fossil-based production, with the degree of benefit depending on electricity source, process efficiency, and product end-use (Abel et al., 2022). For example, electromicrobial production of sustainable aviation fuels from CO₂ and renewable electricity could reduce aviation emissions by 70–90% compared to conventional jet fuel (Sheppard et al., 2022).

Integration with renewable energy systems—particularly intermittent sources like wind and solar—positions electromicrobial systems as flexible chemical storage for excess electricity (Abel et al., 2022; Bakonyi et al., 2022; Rohbohm et al., 2024).

Modular, distributed electromicrobial plants co-located with renewable generation or CO₂ sources minimize transmission losses and enable rapid response to electricity price signals (Bakonyi et al., 2022; Zegers et al., 2025). However, intermittent operation introduces challenges for maintaining stable microbial communities and may reduce overall productivity (Abdollahi et al., 2022; Mills et al., 2022; Rohbohm et al., 2024).

Key Limitations and Open Challenges

Despite significant progress, several fundamental limitations constrain the industrial deployment of electromicrobial systems:

1. **Electron transfer bottlenecks:** Low inward EET rates (typically <1 mA cm⁻² per unit biofilm area) limit current densities and favor large electrode areas per reactor volume, increasing capital costs (Guo et al., 2024; Zhang et al., 2023).
2. **Mass transfer constraints:** Gas-liquid transfer of CO₂ and H₂, and transport of soluble intermediates, limit volumetric rates unless advanced reactor designs (GDEs, flow cells, 3D electrodes) are employed (Cui et al., 2025; Kracke et al., 2021; Pang & Zhu, 2025).
3. **Oxygen and anode chemistry:** OER at conventional anodes conflicts with anaerobic cathodic microbes, requiring complex separation or alternative anode reactions (Abdollahi et al., 2022; Rohbohm et al., 2024).
4. **Community stability and product specificity:** Biofilm diversification and methanogen resurgence require ongoing control strategies to preserve acetogenic or other productive operation (Chandrasekhar et al., 2021; Mills et al., 2022).
5. **Materials and cost:** High-performance nanostructured catalysts improve selectivity but increase material and fabrication costs, affecting scale-up feasibility (Gupta et al., 2024; Herkendell, 2021; Mirea et al., 2025).
6. **Insufficient TEA/LCA validation:** Comprehensive, traceable techno-economic and life cycle analyses tied to experimental metrics are lacking, limiting quantitative assessment of decarbonization potential (Abel et al., 2022; Bakonyi et al., 2022; Sheppard et al., 2022).

VII. FUTURE PERSPECTIVES AND RESEARCH DIRECTIONS

Interface Engineering Advances

Overcoming electron transfer bottlenecks requires integrated advances in protein engineering, mediator design, and electrode functionalization (Guo et al., 2024; Zhang et al., 2023). Priority research directions include:

- Protein engineering of EET conduits: Directed evolution and rational design of multiheme cytochromes, hydrogenases, and formate dehydrogenases to increase electron uptake rates and lower overpotentials (Lai et al., 2023; Rowe et al., 2021; Zhang et al., 2023).
- Immobilized redox polymers: Development of conductive polymer coatings with covalently attached mediators that localize electron carriers at the interface, reducing diffusional losses (Agee et al., 2023; Xu et al., 2021).
- Synthetic biology of electron uptake: Engineering synthetic electron uptake pathways that bypass native EET limitations, such as direct coupling of electrode electrons to central metabolism via engineered quinone pools or flavoproteins (Lai et al., 2023; Mustafa et al., 2025; Zhang et al., 2023).

C2 Relay Optimization

C2 intermediate relay strategies have demonstrated superior performance but require further optimization of both electrochemical and biological modules (Mustafa et al., 2025; Tan & Nielsen, 2022; Zhang et al., 2022):

- Electrocatalyst development: Design of copper-based catalysts with enhanced C2 selectivity (>50% Faradaic efficiency) and stability in biocompatible electrolytes through alloying, surface structuring, and electrolyte engineering (Pan, 2025; Tan & Nielsen, 2022; Zhang et al., 2022).
- Integrated reactor configurations: Development of single-pot or closely coupled electrochemical-biological reactors that minimize intermediate losses and enable continuous transfer of C2 products to fermentation (Cui et al., 2025; Zegers et al., 2025; Zhang et al., 2022).
- Metabolic pathway engineering: Optimization of acetate and ethanol assimilation pathways in

production strains to maximize carbon flux toward target products while minimizing byproduct formation (Boto et al., 2023; Lai et al., 2023; Mustafa et al., 2025).

Materials-Reactor Co-Design

Synergistic optimization of electrode materials and reactor configurations promises substantial performance gains (Gupta et al., 2024; Kracke et al., 2021; Liu et al., 2022; Zegers et al., 2025):

- Low-cost, high-surface-area carbon assemblies: Scalable fabrication of 3D carbon structures via additive manufacturing, templating, or biomass pyrolysis with integrated catalyst deposition (Herkendell, 2021; Kracke et al., 2021; Langsdorf et al., 2021).
- MOF/composite hybrids: Development of conductive MOF-carbon composites with proven long-term stability in aqueous electrolytes and demonstrated biocompatibility (Gupta et al., 2024; Mirea et al., 2025).
- Modular electrode assemblies: Standardized, replaceable electrode modules that enable rapid prototyping, easy maintenance, and incremental scale-up (Herkendell, 2021; Park et al., 2025; Zegers et al., 2025).

Operational Strategies

Advanced operational strategies can improve productivity, stability, and economics (Abdollahi et al., 2022; Liu et al., 2022; Mills et al., 2022; Rohbohm et al., 2024):

- Alternative anodic oxidations: Implementation of waste oxidation (organics, sulfide, ammonia) at the anode to eliminate oxygen production and create integrated waste treatment-chemical production systems (Abdollahi et al., 2022; Chandrasekhar et al., 2021; Horváth-Gönczi et al., 2023).
- Biofilm control loops: Real-time monitoring of biofilm composition via metagenomics or electrochemical signatures, coupled with automated control of operational parameters to maintain desired community structure (Cabau-Peinado et al., 2021; Mills et al., 2022; Song et al., 2021).
- Intermittent operation protocols: Development of start-up, shutdown, and cycling protocols that maintain microbial viability and productivity under intermittent renewable electricity supply

(Liu et al., 2022; Rohbohm et al., 2024; Song et al., 2021).

TEA/LCA Validation

Rigorous techno-economic and life cycle analyses tied to experimental performance metrics are essential for guiding research priorities and assessing commercial viability (Abel et al., 2022; Bakonyi et al., 2022; Sheppard et al., 2022):

- Transparent TEA models: Development of open-source TEA models with clearly defined assumptions, sensitivity analyses, and validation against pilot-scale data (Abel et al., 2022; Park et al., 2025; Sheppard et al., 2022).
- Experimental LCA data: Collection of primary data on material production, energy consumption, and emissions for electrode fabrication, reactor operation, and product recovery (Abel et al., 2022; Bakonyi et al., 2022; Singh et al., 2023).
- System-level optimization: Integration of TEA and LCA with process modeling to identify optimal operating conditions, material choices, and system configurations that minimize cost and environmental impact (Bakonyi et al., 2022; Liu et al., 2022; Park et al., 2025).

VIII. CONCLUSION

Semi-synthetic electromicrobial systems represent a paradigm shift in CO₂ valorization and sustainable chemical manufacturing, coupling the speed and selectivity of electrochemistry with the metabolic versatility of engineered microorganisms. Recent advances demonstrate that C2 intermediate relay strategies, optimized bio-abiotic interfaces, advanced conductive scaffolds, and flow reactor designs can achieve industrially relevant current densities and productivities (Kracke et al., 2021; Song et al., 2021; Zhang et al., 2022). However, significant challenges remain in electron transfer kinetics, mass transport, biofilm stability, and techno-economic validation (Abdollahi et al., 2022; Abel et al., 2022; Guo et al., 2024; Mills et al., 2022; Rowe et al., 2021).

The path toward industrial electromicrobial biorefineries requires integrated advances across multiple disciplines: electrochemistry, microbiology, synthetic biology, materials science, and chemical engineering. Priority research directions include

protein engineering of electron transfer pathways, development of low-cost high-performance electrode materials, reactor designs that eliminate oxygen toxicity, and operational strategies for stable continuous production (Abdollahi et al., 2022; Herkendell, 2021; Lai et al., 2023; Rohbohm et al., 2024; Zhang et al., 2023). Equally important is rigorous techno-economic and life cycle assessment to quantify the decarbonization potential and guide technology development toward commercially viable systems (Abel et al., 2022; Bakonyi et al., 2022; Sheppard et al., 2022).

As renewable electricity costs continue to decline and carbon pricing mechanisms mature, electromicrobial systems are poised to play a critical role in the transition to circular carbon economies. By electrifying biosynthesis and transcending the limitations of natural photosynthesis, these hybrid platforms offer a modular, scalable pathway to produce fuels, chemicals, and materials from CO₂ and renewable energy—transforming waste carbon into valuable products while mitigating climate change.

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