



Dual-Function Electrocatalytic and Macroporous Hollow-Fiber Cathode for Converting Waste Streams to Valuable Resources Using Microbial Electrochemical Systems

Item Type	Article
Authors	Katuri, Krishna;Kalathil, Shafeer;Ragab, Alaa I.;Bian, Bin;AlQahtani, Manal Faisal;Pant, Deepak;Saikaly, Pascal
Citation	Katuri KP, Kalathil S, Ragab A, Bian B, Alqahtani MF, et al. (2018) Dual-Function Electrocatalytic and Macroporous Hollow-Fiber Cathode for Converting Waste Streams to Valuable Resources Using Microbial Electrochemical Systems. <i>Advanced Materials</i> : 1707072. Available: http://dx.doi.org/10.1002/adma.201707072 .
Eprint version	Post-print
DOI	10.1002/adma.201707072
Publisher	Wiley
Journal	Advanced Materials
Rights	Archived with thanks to Advanced Materials
Download date	2024-04-17 19:52:51
Link to Item	http://hdl.handle.net/10754/627745

DOI: 10.1002/((adma.201705955R1))

Article type: Progress Report

Dual-Function Electro-Catalytic and Macroporous Hollow-Fiber Cathode for Converting Waste Streams to Valuable Resources Using Microbial Electrochemical Systems

*Krishna P. Katuri, Shafeer Kalathil, Ala'a Ragab, Bin Bian, Manal F. Alqahtani, Deepak Pant, and Pascal Elias Saikaly**

K P. Katuri⁺, S. Kalathil⁺, A. Ragab, B. Bian, M. F. Alqahtani, and P. E. Saikaly
Biological and Environmental Sciences and Engineering (BESE) Division, Water Desalination and Reuse Center (WDRC), King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

D. Pant
Separation and Conversion Technology, Flemish Institute for Technological Research (VITO), Mol, Belgium

E-mail: pascal.saikaly@kaust.edu.sa

[⁺] These authors contributed equally to this work

Keywords: microbial electrosynthesis, electrochemical membrane bioreactor, CO₂ reduction, electrically conductive porous membrane, artificial photosynthesis

Abstract

Dual-function electro-catalytic and macroporous hollow-fiber cathode has recently been proposed as a promising advanced material for maximizing the conversion of waste streams such as wastewater and waste CO₂ to valuable resources (e.g., clean freshwater, energy, value-added chemicals) in microbial electrochemical systems. The first part of this progress report reviews recent developments in this type of cathode architecture for the simultaneous recovery of clean freshwater and energy from wastewater. Critical insights are provided on suitable materials for fabricating these cathodes, as well as addressing some challenges in the fabrication process with proposed strategies to overcome them. The second and complementary part of the progress report highlights how the unique features of this cathode architecture can solve one of the intrinsic bottlenecks (gas-liquid mass transfer limitation) in the application of microbial electrochemical systems for CO₂ reduction to value-added products. Strategies to further improve the availability of CO₂ to microbial catalysts on the cathode are proposed. The importance of understanding microbe-cathode interactions, as well as electron transfer mechanisms at the cathode-cell and cell-cell interface to better design dual-function macroporous hollow-fiber cathodes are critically discussed with insights on how the choice of material is important in facilitating direct electron transfer versus mediated electron transfer.

1. Introduction

The grand challenges facing society in the current century are water, energy and food security, and climate change. Water, energy and food are interlinked in what is referred to as the water-energy-food nexus.^[1] These challenges are exacerbated due to the rapidly growing

human population, leading to increased resource (water, energy, food and chemicals) consumption with concomitant production of large volumes of ‘used resources’, commonly recognized as waste. These ‘used resources’ could potentially represent an economic value if they are recovered. There is an emerging interest worldwide for resource recovery from waste streams driven by environmental and economic benefits, and the need for a more sustainable society. In this regard, wastewater (i.e., used water) is no longer viewed as just a waste material to treat with negative energy expenditure, but rather as a valuable resource of water, energy, nutrients (nitrogen and phosphorous) and materials (e.g., bioplastics, cellulose fibers, alginate, metals).^[2] Transforming wastewater treatment plants into resource factories is currently a key driver for research and development of next-generation wastewater treatment technologies. Microbial technologies hold great promise for resource recovery from wastewater.^[3] As such, microbial electrochemical systems based on microbial fuel cell (MFC) and microbial electrolysis cell (MEC) (**Figure 1**), offer an opportunity to biologically treat wastewater with the concomitant recovery of energy.^[4, 5] In MFCs or MECs, certain microorganisms known as electricigens transfer the electrons generated during the oxidation of organics in wastewater to the anode. ^[4, 5] The electrons and protons that are generated during oxidation at the anode are utilized at the cathode for production of electricity (in MFC via oxygen reduction reaction; ORR) or H₂ (in MEC via hydrogen evolution reaction; HER) (**Figure 1**).

In a similar context, waste carbon dioxide (CO₂) can be regarded as a resource to produce value-added products. Anthropogenic and industrial activities have led to a rapid rise in the atmospheric CO₂ concentrations (> 400 ppm as of early 2017) leading to increased global warming.^[6] The European Union (EU) emissions of CO₂-equivalents account for about 13%

of the global greenhouse gas (GHG) emitted annually. Moreover, in 2014, the atmospheric level of CO₂ reached concentrations of 397-400 ppm, an increase of about 14% with respect to the last two decades.^[7] Earlier efforts to counter this solely focused on the capture and storage of CO₂, commonly referred to as Carbon Capture and Storage (CCS). However, CCS simply stores CO₂, mostly underground, and does not recognize it as a valuable source of carbon that can be utilized in the production of easily storable chemicals. The latter approach, known as Carbon Capture and Utilization (CCU), is currently being investigated globally. CCU is mainly suitable for CO₂ taken from point sources, such as industrial flue gases, and converting it into commercially valuable products through different approaches such as catalytic conversion, carbonation, and bioconversions using algae or bacteria. Biological CO₂-mitigation, which includes CO₂ fixation by cyanobacteria, green algae, and some autotrophic bacteria, is a well-established practice and is considered more efficient in CO₂ fixation than higher plants due to their fast growth.^[8] However, the practical application is still limited by photobioreactor design and upscaling issues. Gas fermentations have also been explored by using of specific chemotrophic bacteria, such as *Cupriavidus necator* (*Ralstonia eutropha*), for converting CO₂ into biopolymers such as polyhydroxybutyrate (PHB).^[9] More recently, enzyme-electrode based systems have also been used to convert CO₂ into chemicals such as formic acid and alcohols in a process defined as enzymatic electrosynthesis.^[10] A new approach that has emerged in recent years is that of microbial electrosynthesis (MES) (Figure 1), which relies on chemolithoautotrophic bacteria that have the ability to uptake electrons from the cathode of an electrochemical cell to catalyze the reduction of CO₂ into fuels or value-added chemicals at low potentials.^[11, 12] Since MES use electricity as the energy source, it can be coupled to renewable energy sources (e.g., wind and solar), allowing for a fast

switch on/off or adjustments in capacity (**Figure 2**). The concept of MES thus directly addresses the circular economy challenge, taking advantage of the excess electricity from renewable sources to maintain electricity-driven bioproduction. Bioelectrochemistry, of which MES is a part, is a burgeoning area with an active scientific community exploring a multitude of research avenues.^[13]

Cathodes are integral parts of any microbial electrochemical system, consequently improvements in the cathode material and architecture can lead to significant enhancements in the performance of these systems. Several cathode materials (carbon-based, metal-based and composite materials made of carbon and metal) and configurations (planar material such as plate, rod, paper, cloth and mesh; three-dimensional porous materials such as foam and felt) have been employed in microbial electrochemical systems that witnessed improved performances in terms of HER and biofuel/chemical productions; these are discussed in detail in many existing reviews and so they will not be the focus of this progress report.^[14, 15] In this progress report, we will only focus on the recent developments of the three-dimensional (3D) electrically conductive, catalytic and macroporous hollow-fiber cathode, herein referred to as CCPHF cathode, as a promising advanced material for engineering microbial electrochemical systems to maximize their potential in addressing water and energy sustainability and mitigating climate change. The unique aspect of these cathodes is that, in addition to their role as cathodes for HER, they can also function as a porous membrane for filtration of treated water and direct CO₂ delivery to microbial catalysts in MES. Importantly, the two functions can occur simultaneously without interfering with each other. Also, the hollow fiber architecture of the CCPHF cathode with high surface-area-to-volume ratio is desirable for reducing the footprints required for scale-up of the technology.

The progress report begins with a description of the superior performance of microbial electrochemical systems with dual function macroporous hollow-fiber cathode architecture over macroporous flat cathodes for water and energy recovery from wastewater. The importance of porous hollow fiber cathode architecture in overcoming some bottlenecks in the application of MES for CO₂ reduction is also discussed. Future research aspects to overcome technological bottlenecks in the engineering of these porous hollow fiber cathodes are introduced. The report also sheds light on the importance of understanding microbe-cathode interactions and electron transfer mechanisms at the cathode-cell and cell-cell interface to better select cathode materials for the design of CCPHF cathodes for MES applications.

2. Dual-Function Macroporous Cathode Architectures for Simultaneous Recovery of Clean Water and Energy from Wastewater

2.1. Macroporous Flat Sheet Cathode vs. Macroporous Hollow Fiber Cathode Architecture

The aerobic membrane bioreactor (MBR) is the state-of-the-art biotechnology for biological wastewater treatment and reuse, where microfiltration (MF) or ultrafiltration (UF) membranes are used to separate suspended solids and bacteria from the biologically treated water with a considerable energy penalty (1-2 kWh/m³).^[16] A large fraction of the energy used to operate MBRs is due to aeration to supply oxygen for bacterial respiration, as well as to scour the surface of the membranes for fouling control. Therefore, there is a need to develop more sustainable biotechnologies based on anaerobic processes to maximize wastewater resource recovery whilst reducing energy demand. Anaerobic processes based on MFCs or MECs offer an alternative approach to biologically treat wastewater with concomitant recovery of the

inherent chemical energy in wastewater. However, MFCs or MECs alone cannot produce high-quality water suitable for reuse, for that purpose they have to be integrated with membrane filtration processes. The idea of developing hybrid MFC/membrane filtration systems has been considered; however, these systems do not present a true integration of these two processes (i.e., biological treatment and electricity generation processes were separated from the filtration process).^[17] Full integration requires the development of dual function cathodes to function as both cathode (for ORR or HER) and porous membrane (for the filtration of the treated water). Dual function cathodes have several advantages including the reduction in operation and capital cost, and the footprint required for treatment.

The concept of developing MF or UF flat sheet cathodes (submerged or as air cathode) for MFC application has been considered by several research groups.^[18-30] For example, our group developed an electrically conductive flat sheet UF membrane by dispersing multi-walled carbon nanotubes (MWCNTs) as a multilayer on top of a polyester nonwoven membrane base.^[22] The developed UF membrane functioned as a cathode for ORR and a membrane to filter the treated water in a single-chambered air-cathode MFC. This novel and truly integrated MFC/membrane filtration system avoided the need for a separate membrane module while achieving a high-quality permeate comparable to conventional MBRs. The majority of these custom-built dual function cathodes were fabricated with nitrogen-doped carbon nanotubes (CNTs), polypyrrole (PPy), reduced graphene oxide (RGO)/PPy, catalysts (C, Mn, Fe and O) and RGO using either a porous polymeric, carbon fiber or stainless steel (SS) mesh as substratum (**Table 1**).

Dual-function cathodes also hold benefits for membrane biofouling mitigation. Membrane biofouling is an unavoidable phenomenon in membrane filtration processes, contributing

significantly to both operation and capital costs that arise from the need to clean or replace the membranes. Recent studies showed that carbon-based electrodes reduce O_2 to H_2O_2 via a $2e^-$ reduction mechanism^[31] while platinum (Pt) and Fe-based cathodes reduce O_2 to H_2O via a $4e^-$ reduction mechanism^[32]. Therefore, the fabrication of carbon-based flat sheet MF or UF cathodes is advantageous in MFC-MBRs, as the *in-situ* chemical cleaning by H_2O_2 generated on the surface of the membrane during the ORR can mitigate membrane biofouling.^[33]

A major disadvantage of using MF or UF flat sheet cathodes is their low surface-area-to-volume ratio. Increasing the packing density of the cathode is a critical aspect of the design of microbial electrochemical systems for practical applications in wastewater treatment. Additionally, the current density in MFCs is low and has to be increased considerably for commercial applications, whereas MECs have already been applied at a commercial scale as their current density can be increased by increasing the applied voltage.^[34] To overcome the limitations of cathode packing density, we have recently developed a novel anaerobic biotechnology by integrating CCPHF cathodes made of pure nickel (Ni) with the operating principles of MEC to recover clean water for reuse and energy as biogas from wastewater, in what is referred to as an electrochemical membrane bioreactor (EMBR) (**Figure 3**).^[4] In addition to water and energy recovery, the hollow fiber architecture of the cathode with small radial dimensions provides a high surface-area-to-volume ratio, combining compactness, a simple and modular reactor design, and high performance.^[35] Biofouling in the EMBR system was mitigated via the *in-situ* cleaning by the hydrogen bubble formation on the cathode surface. Other factors associated with HER activity which can contribute to biofouling mitigation include the localized high pH at the cathode surface due to proton consumption, low cathode potential, and electrostatic repulsive forces between the negatively charged

CCPHF cathode and similarly charged foulants (**Figure 4**).^[4, 16, 35] Therefore, the EMBR is a perfect example of integrating advancements in material science with applied microbiology and electrochemistry to create a novel biotechnology that addresses two grand challenges facing society: providing an adequate supply of clean freshwater and energy to the increasing world population.

Porous metal-based hollow fibers composed of copper (Cu) have also been used recently as cathodes in aqueous electrolytes for CO₂ reduction.^[36] Unlike other HER and CO₂ reduction electrocatalysts using precious metals, the CCPHF electrodes were made entirely using earth-abundant and non-precious metal catalysts, like Ni and Cu. Both the Cu and Ni CCPHF cathodes were fabricated using a combined phase-inversion/sintering method^[4, 36], and the same fabrication procedure can be applied to other earth-abundant metal catalysts like iron (Fe). The fabrication of these metal-based CCPHF cathodes is simple and cost-effective, and the material is robust under the harsh conditions (for example, environments associated with the cathodic reactions); and the CCPHF cathodes can be eventually scaled-up for EMBR and MES application (see **Section 3.2**) for harnessing resources from waste streams. Nevertheless, the main disadvantage of using these metal-based CCPHF cathodes in the EMBR system is their default formation of pore structure, size, and density during fabrication. These parameters ultimately affect the filtering properties of the CCPHF cathode, such as flux and recovery of high-quality permeate due to the passage of bacteria through $\geq 1\mu\text{m}$ pores. Further optimization of the fabrication procedure is needed to generate fibers with higher pore densities and smaller pore sizes ($< 0.5\ \mu\text{m}$) to yield higher quality permeate. Another bottleneck of metal-based CCPHF cathodes is the possibility of metal leaching into the solution. To address this, we synthesized a graphene layer directly on the Ni CCPHF cathode

through chemical vapor deposition (CVD) technique.^[16] The graphene layer served as the HER catalyst instead of Ni. The graphene CCPHF cathode exhibited a similar HER overpotential (~ -0.5 V) compared to the Ni CCPHF cathode. At -1.0 V, the maximum current density of the graphene CCPHF cathode was only 20% that of the Ni CCPHF cathode. Co-doping graphene with earth-abundant metal^[37, 38] or non-metal^[39] HER catalysts (such as nitrogen and sulfur) could serve to further improve the HER performance of graphene CCPHF cathodes.

Although CCPHF electrodes have the potential to solve some intrinsic bottlenecks related to membrane processes (membrane fouling) and microbial electrochemical systems (cathode specific surface area), they must be affordable and easily fabricated at a large scale. Porous polymer-based hollow fibers are flexible, cheaper and simpler to manufacture using conventional polymeric membrane manufacturing methods (i.e., phase inversion), as well as easier to integrate into modules. Phase inversion is not difficult to upscale and is the most applied method to manufacture polymeric membranes.^[35] Also, protocols are well established for tuning the membrane properties (e.g., pore size and pore density) to improve the efficiency of the separation process in EMBR systems. The following section describes the possible routes for fabrication of CCPHF cathodes using polymeric membranes as a platform.

2.2. Polymer-Based CCPHF Cathode

Transforming porous polymeric hollow fibers into CCPHF electrodes without affecting the structural integrity of the membrane architecture is an attractive approach. However, most of the polymers used in the membrane casting are electrically non-conductive, and the few existing conductive polymers^[40] such as PPy, polyacetylene, and polythiophene are difficult

to process in solution. Recently, there has been an increased interest in the development of electrically conductive polymeric membranes and their integration with electrochemical techniques for fouling mitigation in membrane filtration processes (e.g., MF, UF, nanofiltration and forward osmosis).^[41] Reviews of recent developments in the fabrication of electrically conductive polymeric membranes for fouling mitigation in water treatment and desalination are available.^[40, 42] Generally, the fabrication of these electrically conductive polymeric membranes involved either mixing electrically conductive materials (like CNTs) with polymers and then membrane casting, or layering thin films of the electrically conductive materials on pre-casted polymeric porous membranes. However, these fabrication approaches are mainly restricted to the development of flat-sheet polymeric membranes, which suffer from low surface-area-to-volume ratio as previously mentioned.

Combining high electrical conductivity and catalytic activity with the processability of porous polymeric hollow fiber is a challenge. Recently, we demonstrated for the first time the preparation of polymeric CCPHF cathodes by fabricating porous fluorinated polyoxadiazole hollow fibers by phase inversion, followed by the deposition of a very thin Pt layer on their outer surfaces by atomic layer deposition (ALD), to render the porous fluorinated polyoxadiazole hollow fibers electro-catalytic.^[35] These porous hollow fiber cathodes served as a MF membrane to block passage of suspended solids and bacteria, while the outer surface was electro-catalytic serving as a cathode for HER. The developed polymeric CCPHF cathode was applied in an EMBR for clean water and energy recovery from low-organic strength wastewaters. This novel approach of polymeric CCPHF cathode fabrication using ALD allows precise tuning of pore size and pore architecture to effectively block the passage of bacterial cells during the filtration process, and, consequently high-quality water (permeate)

with turbidity of < 0.1 nephelometric turbidity units, enabling reclamation of treated effluent. Additionally, ALD is a robust deposition method for uniform and precise catalyst loading on 3D hollow fibers as thin films. Our results showed that 200 ALD cycles of Pt formed a thin layer (26 ± 5 nm) of nano-sized catalysts without blocking the pores; this thickness was sufficient to achieve excellent electronic conductivity and electrochemical activity. The HER activity of the CCPHF cathodes fabricated with 200 ALD cycles of Pt ($0.2 \text{ mg Pt cm}^{-2}$) showed similar electrochemical performance as observed with the benchmark platinum/carbon (Pt/C) cathode ($0.5 \text{ mg Pt cm}^{-2}$) in MEC mode of operation.^[35] These results are quite promising for facilitating cathodic reaction in EMBR with a minimal amount of catalyst concentration, i.e., 60% lower than the Pt loading of benchmark cathodes. The Pt nanostructures (5 nm) in the catalyst layer increased the number of active catalytic sites per mass of catalyst, leading to a high HER activity with low Pt loading and, thus minimizing the costs associated with the use of precious metal catalysts.

The ALD technique is not limited to Pt; earth-abundant and inexpensive HER catalysts like Ni are viable alternatives to precious metal catalysts. However, using this technique poses some challenges in CCPHF fabrication. Since the processing temperature within the ALD coating chamber can reach as high as $180 \text{ }^\circ\text{C}$, this limits its application to heat resistant polymeric membranes (e.g., fluorinated polyoxadiazole). Also, currently there is no commercially available ALD device that enable the fabrication of polymer-based CCPHF cathodes at a large scale. Additionally, the intrinsic low stability (chemical, thermal and mechanical) and non-electrical conductivity of polymeric hollow fiber membranes limits the usage of traditional surface coating methods such as CVD and electrochemical deposition to transform them into CCPHF electrodes. These traditional surface-coating methods may not

allow for the required precise formation of a thin electro-catalyst layer on the 3D hollow fiber membranes, leading to pore blockage.

An alternative for making CCPHF cathodes is using ceramic hollow fiber membranes as support material (i.e., substratum) for immobilizing the desired electro-catalyst layer peripherally as a thin layer. Ceramic membranes can be easily fabricated as hollow fiber membranes using conventional polymeric membrane manufacturing equipment and methods. Although ceramic membranes are more expensive than polymeric membranes, their high mechanical stability, resistance to harsh environments (high temperatures, chemical degradation, pH, etc.), and semi-conducting electrical behavior are advantageous in creating CCPHF cathodes using various surface modification techniques. [Section 2.3](#) below describes possible routes for fabrication of CCPHF cathodes using ceramic hollow fiber membranes as a platform.

2.3. Ceramic-Based CCPHF Cathodes

Ceramic membranes enjoy a rich abundance of raw materials with high stability in acidic and alkaline environments. The filtration and gas separation properties of several ceramic membranes, such as aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), silicon dioxide (SiO_2) and their composites, have been widely studied.^[43] However, the electric insulation of ceramic hollow fiber membranes is a big challenge for its use as CCPHF cathode material in EMBR systems. Below we propose several strategies to overcome this challenge.

The first approach is to deposit a thin layer (< 300 nm) of metal catalysts onto the surface of ceramic hollow fiber membranes. Non-expensive metal catalysts, including Ni, Fe, and

cobalt (Co), usually possess high conductivity and high HER catalytic activity^[44], and thus are ideal for thin-film catalyst deposition. ALD is a fast-growing technique for ultrathin film coating.^[35] Several studies have already explored the possibility of metal deposition on ceramic particles or flat substrates using ALD. Chae et al.^[45] used ALD to deposit a thin film of Ni on TiN/SiO₂/Si wafers by sequentially supplying Ni(cp)₂ precursor, water vapor and hydrogen. Espejo et al.^[46] further developed the ALD process to coat NiFe thin films on Si wafers with 110 nm SiO₂ layer on top. In 2013, Gould et al.^[47] utilized alumina powders as Ni thin film support, which opened the door for ALD deposition of non-expensive metals onto ceramics. The ALD approach for depositing a thin film of metal catalyst is quite promising if parameters are optimized to develop a uniform and conductive layer on ceramic hollow fiber membranes. However, as previously mentioned, this requires an ALD infrastructure for the fabrication of ceramic-based CCPHF cathodes at large scale. Apart from ALD, various physical vapor deposition (PVD) techniques have been extensively used to synthesize thin metallic/alloy films, such as sputtering^[48, 49], flash evaporation pulse laser deposition^[48], and electron beam deposition.^[50] The main challenges of these techniques are usually uniformity and composition control throughout the thin film, commonly using Si wafers as substrates due to their compatibility with Micro-Electro-Mechanical Systems (MEMS) technology. Also, electroless plating has been widely used for metal coating on ceramics.^[51, 52] By carefully tuning the plating time and components, uniform thin layers of metals could be deposited onto ceramic membrane surfaces without blocking the pores.^[51]

The second approach is depositing CNTs on the surface of ceramic membranes. It has been reported that CNTs can directly transfer electrons from electrode to microbes.^[53] Thus, CNT coatings on porous hollow fibers (**Figure 5**) are believed to greatly enhance the

coulombic efficiency and catalytic properties of electrode materials in microbial electrochemical systems. Mazumder et al.^[54], deposited both molecular sieves (which could be used to enhance CO₂ adsorption) and CNTs via catalytic chemical vapor deposition (CCVD) methods onto a porous ceramic plate with an average pore size of ~10 nm. A high yield of CNTs (~17%) was achieved, forming a thick conductive layer on the ceramic surface. CNTs could also be deposited onto the ceramic membrane surface via spray coating^[55] or vacuum-filtration.^[56] CNT-Polyvinyl alcohol (CNT-PVA) layers with excellent conductivity and stability were spray coated on flat ceramic membranes, which served as Joule heaters in membrane distillation.^[55] Fan et al.^[56] mixed CNTs with polyacrylonitrile (PAN) to cast CNT layers onto a porous ceramic hollow fiber substrate via a vacuum-filtration process. After pyrolysis in a hydrogen atmosphere, the conductive hollow fiber membrane exhibited effective membrane fouling mitigation in an electric field. With electric field driving the low membrane fouling, this ceramic/CNT hollow fiber membrane could find its application in EMBR. The plasma enhanced chemical vapor deposition (PE-CVD) reactor, referred to as “the Rolls-Royce of R&D facility for carbon nanostructures”, has been successfully used for growing mono and multi-layer graphene and CNTs on substrates. The precise layer formation by PE-CVD enhances the electrical conductivity of the carbon framework, which is one of the prerequisites for minimizing the electrical resistance of CCPHF electrodes. This approach is, of course, advantageous in forming an electrically conductive carbon foundation layer on non-conductive and porous 3D structures like ceramic hollow fiber membranes.

CNT deposition on porous ceramic hollow fiber membranes is also essential to form 3D structures on the membrane surface with the possibility of further surface modifications like catalyst decoration^[57, 58] and functionalization^[59] (Figure 5). Many non-noble metal catalysts

have been developed and encapsulated in CNTs,^[38] to achieve efficient catalytic properties for HER. Ni, Co, and Fe nanoparticles and their composites are the most common alternatives for HER as they are highly abundant.^[57, 60, 61, 62] Deng et al.^[57] reported one kind of FeCo alloy catalyst onto CNTs with long-term durability to obtain ~70 mV onset overpotential and optimized electronic structure of CNTs, the performances of which could compete with commercial 40% Pt/C cathodes. CoP^[61] and Ni₂P^[62] nanocrystals, as well as Co/FeS₂ nanosheets^[57], hybridized with CNTs also exhibited similar low onset overpotentials (< 120 mV). Thus, high-efficiency HER could be expected using ceramic-based CCPHF cathodes.

In this context, it is worthy to highlight the role of different electrochemical techniques to improve cathode design and evaluate their performance.^[35, 63, 64] For example, electrochemical techniques such as linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were used as powerful tools to detect defects during the fabrication process of custom built polymer-based CCPHF cathodes and improve their design.^[35] The EIS technique can provide insights on the electron transfer resistance through the CCPHF cathode, and this information can aid in fine-tuning fabrication processes.^[35] LSV analysis is useful to determine the onset potential of different HER catalysts (carbon- or metal-based) used in fabricating CCPHF cathodes^[16, 35] and to assess their electrochemical performance through the generation of Tafel plots. The Tafel slope and exchange-current density extracted from the Tafel plot provide an indication of the performance of HER electrocatalysts. Understanding ORR kinetics is crucial to design high-performing MF or UF flat sheet cathodes for MFC-MBR applications. Typically, ORR follows two pathways for O₂ reduction; 2e⁻ reduction pathway (H₂O₂ production) and 4e⁻ reduction pathway (H₂O production). Rotating ring disc electrode (RRDE) assembly is extremely useful to determine these pathways.^[63] Similarly,

instrumental techniques like porometer and porosity measurements (ϵ) act as essential tools to assess the pore size distribution and pore density of the CCPHF cathodes. Reliable performance evaluation is vital for comparability and real-world applicability to push forward the improvement and optimization of CCPHF cathodes for wastewater resource recovery, or CO₂ conversion to value-added products, which is the main topic of [Section 3](#).

3. Converting Waste CO₂ to Value-Added Products by MES

3.1. Natural Photosynthesis vs. MES

Natural photosynthesis is a unique process in which sunlight is harvested to convert water and CO₂ into energy in the form of organic molecules (chemical bonds).^[65] It is worth noting that 1 hour of sunlight reaching Earth is enough to support anthropogenic energy demands for an entire year.^[66] Photosynthesis proceeds through the combination of two different photosystems, photosystem II (PSII) and photosystem I (PSI). PSII triggers water splitting by producing oxygen and hydrogen equivalents with the aid of light, while PSI accelerates the energy of PSII-energized electrons/protons using light to fix CO₂. The electrons generated by water splitting in PSII move to PSI through a series of protein networks, mainly via cytochromes. Indeed, the natural photosynthetic system is a paradigm to draw a blueprint for the development of artificial photosynthetic systems such as MES to produce energy from CO₂ feedstock ([Figure 2](#)). However, natural photosynthesis suffers from multiple drawbacks that deteriorate the efficiency of the system.^[67] Potential mismatches in the photosynthetic systems lower the efficiency of photosynthesis by the poor capture of incident sunlight (0.25 – 1 %).^[68] Here, MES offers more efficient solar energy capture to produce value-added products from CO₂.^[11] MES mimics photosynthesis by employing photovoltaics for water

splitting at the anode and to provide electrons to electroautotrophs for CO₂ fixation at the cathode (Figure 2). The solar-to-electricity efficiency of photovoltaics is more than 40%, and their cost is expected to reduce significantly in the near future^[68], which can be beneficial to set up low-cost MES systems. The molecular machinery involved in photosynthesis shares many similarities with photovoltaic-powered MES such as in light harvesting, electron transfer and CO₂ fixation. A comparison of the molecular machinery of photosynthesis and MES gives us an opportunity to address the inefficiency of photosynthesis, and this information can be helpful to design an efficient MES system for fixing CO₂ to fuels/chemicals. The MES technology allows us to replace the low efficiency CO₂-fixing Calvin cycle with a faster and more efficient carbon fixation cycle (e.g., Wood–Ljungdahl pathway).

Recently there is an emerging interest in coupling sunlight with microorganisms to reduce CO₂ to high-value chemicals (Figure 6).^[69, 70, 71] For example, Liu et al.^[70] developed a water splitting-biosynthetic system with CO₂ reduction by wiring an H₂-generating inorganic ‘artificial leaf’ with an H₂-oxidizing autotrophic microbe, *Ralstonia eutropha*. The H₂ produced by the inorganic leaf was consumed by *R. eutropha* to synthesize liquid fuels. This proposed biosynthetic system exceeded the efficiency of natural photosynthesis. Sakimoto et al.^[72] developed an *in-situ* synthesized cadmium sulfide (CdS)-bacteria hybrid system to produce acetic acid from CO₂ by harvesting light. This study demonstrated that the light harvesting capability of semiconductors could trigger bio-catalytic activities of bacteria to produce high-value chemicals and fuels. Taken together, these results show that integration of sunlight, inorganic catalyst and microbial catalyst for the production of chemicals/fuels from

CO₂ feedstocks has a great potential in the field of green energy and climate change mitigation.

From a biological perspective, a major challenge to overcome in microbial electrochemical CCU using the MES approach is increasing the biomass density of electroautotrophs (i.e., microbial catalyst), and hence biocatalysis efficiency, on the cathode surface. Generally, a biocompatible and high surface area cathode is advantageous for the growth of electroautotrophs as well as for increasing biomass density.^[73] The high surface area associated with an appropriate cathode architecture enables a reduction of cathode overpotential^[74], and also improves the current density and carbon capture efficiency of MES.^[73] Cathode surface area is one important design aspect, another is the development of a cathode architecture with a three-phase interface (i.e., between CO₂ gas, cathodic biofilm and electrolyte) to achieve a balance between various bio-physico-chemical phenomenon during microbial electrochemical CCU. This is important because gas-liquid mass transfer is one of the limiting factors in MES for CO₂ reduction, mainly because of the low solubility of gaseous CO₂ in solution and the fact that CO₂ is only available to electroautotrophs in aqueous forms (i.e., CO_{2(aq)}, HCO₃⁻, and CO₃²⁻) (**Figure 7**). In the following section we present a new cathode architecture, recently proposed by our group for MES application,^[75] based on the concept of CCPHF cathode developed for EMBR application (**Section 2.2**), to address the gas-liquid mass transfer limitation in MES.

3.2. CCPHF Cathode Architecture and Materials for CO₂ Adsorption to Enhance CCU in MES

Recently, the application of Cu-based CCPHF cathodes in the electrochemical conversion of CO₂ presented significant advantages over conventional approaches.^[36] The CO₂ gas purged through these hierarchically structured materials with a three-phase interface lead to a ca. two folds increase in cathodic current density. Decent CO₂ to CO conversion efficiencies (~72% Faradaic efficiency) with very high CO production rates comparable to those achieved using noble metals were obtained using this approach.

Our group has proposed the application of Ni-based CCPHF cathodes in MES for microbial electrochemical CCU.^[75] The CCPHF cathode acts as an electron donor (direct or indirect through H₂) for electroautotrophs as well as a diffusive material to facilitate direct delivery of CO₂ gas into the biocathode through the pores in the hollow fibers (**Figure 8**). The use of CCPHF cathodes in MES research is a significant breakthrough. The high specific surface area of the CCPHF cathode maximizes the diffusion of CO₂ gas, and the high surface-area-to-volume ratio of the CCPHF cathode architecture solves the issue of cathode packing density for large-scale applications. Also, direct delivery of CO₂ gas to the biofilm attached to the cathode avoids the gas-liquid mass transfer limitations that occur in other MES configurations where gaseous CO₂ is bubbled into the solution. Using the Ni-based CCPHF cathode we observed a Faradic efficiency of 77 % for the production of CH₄ from CO₂ through hydrogenotrophic methanogens when CO₂ was delivered directly through the pores of the hollow fiber cathode, compared to 3 % when gaseous CO₂ was bubbled into the solution.^[75] Most importantly, using CCPHF cathodes make the MES process highly attractive for on-site CCU of CO₂ gas generated from various industrial sources. In general, delivering CO₂ directly through the pores of the hollow fibers decreases the pH of electrolyte^[76], however, this is counterbalanced by the consumption of protons at the cathode for HER, thus

maintaining a pH balance at the biofilm-electrolyte interface.

Integrating CNTs^[73] or metallic nanoparticles for HER such as Cu nanoparticles^[77] on porous hollow fibers (Figure 5) could improve their performances in MES. Metal nanoparticles offer a high surface area and stability for the HER catalytic activity^[35], leading to a high microbial electrosynthesis rate of desired products if the major pathway of electron transfer from the cathode to microbial catalysts happens through H₂. On the other hand, CNTs provide high conductivity and excellent biocompatibility^[78], which allow for better attachment and growth of microbial catalysts on the cathode surface.^[73] Recently, Cui et al.^[79] described an inexpensive, and one-step method to fabricate ferric oxide graphitized nanostructures on carbon felt to create a 3D hierarchical porous structure electrode for increasing MES efficiency. This effective strategy might provoke further research to find new simple methods for fabricating nano-metal particles, to reduce cost and time.^[79]

Using cathode electrodes made of composite materials (e.g., conformal coating of a thin layer of HER metal (e.g., Ni) on carbon electrode) is advantageous in enhancing MES-based CCU. The localized H₂ generated through HER, which is an indirect route responsible for microbial electrochemical CCU, favors biomass growth and activity of microbial catalysts during the MES process. Also, the composite material can increase both the biocompatibility and electrical conductivity of cathodes.^[73, 80] For example, SS felt coated by carbon achieved a highly biocompatible surface;^[81] carbon cloth decorated with metallic nanoparticles such as gold (Au), palladium (Pd), and Ni reached high electrosynthesis rates.^[78] However, selection of the fabrication techniques for making composite cathodes depends on the architecture scale. Also, various factors that affect the composite cathode fabrication, like doping strength and homogeneity of metal deposition, need to be taken into consideration.

For the practical application of CCPHF cathode for microbial electrochemical CCU in MES, the input CO₂ source may be the atmosphere or combustion gases. Several separation and adsorption techniques have been developed to capture and segregate CO₂ from mixed gases, such as chemisorption^[82], adsorption^[83], membranes^[84] and microbial systems.^[85] However, most separation processes come with irreversibility, which leads to inefficiencies. CO₂ storage and conversion in porous materials such as molecular sieves and Metal–Organic Frameworks (MOFs) have thus become an attractive option for environmental applications and resource recovery in closed-volume settings.^[86] For the MES applications, gas separation through a thin layer of molecular sieves or MOFs may provide a higher concentration of CO₂ for resource recovery.

Zeolites, microporous aluminosilicate materials, are the most widely used molecular sieves for CO₂ adsorption, which is basically related to van der Waals forces. Even in low-pressure gas conditions, zeolites were reported to have complete reversibility, high CO₂ uptake capacity, selectivity and thermal stability.^[87] Hundreds of zeolite materials have been tested for their capability for CO₂ separation from N₂, H₂ and CH₄. Such high selectivity and adsorption of CO₂ over N₂ could be used for the formation of higher CO₂ concentration at the interface between microbes and cathodes, and the slow release of CO₂ for microbial consumption would probably promote the recovery efficiency in MES. Also, mild temperatures for CO₂/N₂ separation, ranging from 273 K to 313 K, indicate the great potential of application for CO₂ adsorption and recovery in MES.

Most zeolite materials based on aluminosilicate could be biocompatible because of their inherent high stability and excellent cell adhesion.^[88] Several zeolite materials have thus found their application in microbial electrochemical systems, serving as anode^[89], cathode^[90]

or proton exchange membrane^[91] in MFCs. Wu et al.^[89] modified graphite felt anodes with NaX in dual-chamber MFCs and achieved a maximum power density as high as 215.4 mWm⁻², 152.1% higher than the unmodified anode. Scanning electron microscope (SEM) images exhibited the improved SSA, biocompatibility and superhydrophilicity of the NaX zeolite-modified anode, for thick anode biofilm formation. Another example of NaX zeolite utilization for biocathode modification in MFCs was also reported by Wu et al.^[90] Reduction of hexavalent chromium (Cr(VI)) was examined together with current production after HNO₃ pretreatment of NaX coated anode. Higher Cr(VI) removal rate ($10.4 \pm 0.28 \text{ mgL}^{-1}\text{h}^{-1}$) was achieved compared to the unmodified graphite felt, which was attributed to the strong affinity of NaX zeolite particles for microorganisms and Cr(VI) ions. These studies demonstrated that modifying electrode materials in microbial electrochemical systems with zeolites could greatly enhance the reactor performance without loss of conductivity and biocompatibility.

MOFs are recently emerging as a new type of microporous materials, with a permanent porosity and functional linkers. The potential applications of MOFs are similar to that of zeolites, including the most conventional areas of gas storage, separation, and heterogeneous catalysis for CO₂ conversion.^[92] MOFs usually possess a flexible framework due to bond angle, linker twisting and cluster deformation, which means surface modification or functionalization could occur and open metal sites, like Mn, Fe, Co, are accessible for CO₂ adsorption and catalysis. Recently, MOFs with open Co or alloy sites were developed as cathodic catalysts for bioelectricity generation in MFCs. You et al.^[93] successfully synthesized a new type of MOF-derived electrocatalyst (ZIF-67, water-resist) containing Co and N-doped carbon in a single-chamber MFC, achieving a maximum power density of 1665 mW/m² attributed to increased active sites and improved mass transfer by the introduction of

N and Co species. Tang et al.^[94] further developed this kind of MOF material by dual metal and nitrogen co-doping on graphite carbon matrix (M/CoNC). The Ni/CoNC catalyst exhibited the best ORR performance and excellent stability in MFCs, producing a power density of 4335.6 mW/m² with a durability of more than 755 h.

Although both molecular sieves and MOFs have exhibited great potential as cathode catalysts, studies utilizing these microporous membrane materials for microbial electrochemical CCU in MES are lacking due to their low conductivity and the instability of MOF membranes in water. However, based on the understanding that MOF structures must possess strong bonds and steric hindrance to prevent water molecules from intrusion^[95], research on water stable MOFs is booming with plenty of water stable MOFs synthesized in recent years.^[96]

A practical route for integrating MOFs or molecular sieves for microbial electrochemical CCU in MES is to fabricate CCPHF cathodes with continuous water-stable MOF or molecular sieve layers grown on the inner or outer surface^[97] (Figure 5). The deposition of molecular sieves and MOF membranes for CO₂ adsorption on the outer layer of CCPHF cathode could enhance the CO₂ concentration at the abiotic-biotic interface, which greatly increases CO₂ availability for bacterial growth and conversion. Another advantage of metal-doped zeolite or MOF coating on CCPHF cathodes is that they provide extra CO₂ activation sites for CO₂ conversion, which is expected to further reduce the energy input in MES. Since CO₂ is quite stable at room temperature (C=O bonding energy: 750 kJ/mol), efficient CO₂ capture and activation is a prerequisite for high CO₂ recovery. Several cheap metal-based MOFs have been demonstrated to exhibit high catalytic properties for CO₂ activation and reduction in electrochemical systems, including CuZnDTA^[98], M-MOF-74 (M=Co, Ni, Zn)^[99], CR-

MOF^[100], and Fe-Porphyrin-Based MOF^[101]. Most of these materials coated on the surface of electrically conductive substrates show very high selectivity for CO₂ recovery over H₂ and high surface coverage of catalytic sites in electrochemical systems. However, these electrochemical systems for CO₂ reduction usually have lower faradaic efficiency (FE) ^[102] than MES systems. Integrating MOFs or molecular sieves, with their excellent CO₂ adsorption and activation capabilities, with CCPHF cathodes might increase the coulombic efficiency and CO₂ conversion rates in MES.

The traditional thinking of developing efficient electrodes for MES has mainly focused on electrode type (for improved biocompatibility, cell adherence and superior intrinsic conductivity) and architecture (increasing specific surface area and enhancing mass transfer), while ignoring other crucial phenomena taking place at the abiotic-biotic interface such as how electrode topography and material can induce molecular changes in microbes, and the electron transfer mechanisms occurring at the cathode-cell and cell-cell interface as they are the driving force for all the relevant product-forming reactions. Therefore, a prior understanding of the role of cathode surface properties and material on microbial metabolism and the mechanisms of electron transfer at the cathode is required to rationally design more efficient and effective cathodes for MES, and currently, this critical information is largely neglected or underestimated in the field of microbial electrochemical systems. In the subsequent two sections (i.e., [Sections 3.3](#) and [3.4](#)) we will critically discuss the role of electrode material and surface properties on the metabolism and electron transfer processes of microbes, and we will propose some candidate cathode materials that can facilitate direct electron transfer between cathode-cell and cell-cell interface.

3.3. Understanding Surface-Microbe and Material-Microbe Interactions: A Key to Rational Design of High-Performing CCPHF Cathodes for MES

Understanding the molecular mechanisms involved in the interaction of microbes with materials and solid surfaces is the key to the rational design of novel and more efficient cathodes for MES. Numerous studies have shown that solid surfaces can regulate cell response and influence the social behavior of bacteria.^[103] Therefore, to develop high-performing electrodes for MES, it is pivotal to get a prior understanding of how to design an electrode surface to induce a desired behavior in microbes (e.g., ability to reduce CO₂). Nanofabricated structures can be employed as toolkits to investigate the role of surface topography on bacterial metabolism.^[104] Rizzello et al.^[105] revealed nanoscale topography-induced variations in the morphology, genomics, and proteomics of bacteria. Au substrates with various nano-roughness were used to investigate the role of surface topography on bacterial biological responses. The study showed that nano-roughness critically altered the protein expression for biosynthesis, metabolic pathway and peptide transport. Similarly, a study by Helbig et al.^[106] revealed that bacteria could sense subtle structural modifications on a solid surface and can adapt their metabolism accordingly. Similarly, Hsu et al.^[107] reported that surface topography can influence the expression of different types of appendages that might be involved in biofilm formation. Surface roughness is also believed to stimulate bacteria-surface interactions during biofilm formation.^[108] An elegant study by Jeong et al.^[109] revealed that bacteria can recognize nano-topography during biofilm formation. The authors employed precisely controlled Si nanowire arrays developed on a Si substrate to visualize bacterial attachment, and it was observed that the majority of bacterial cells attached to the Si

nanowires instead of the Si substrate (**Figure 9**). This observation sheds light on the fact that bacterial attachment is very sensitive to surface structures and properties.

Graphene and CNT-based materials are commonly used as electrodes in microbial electrochemical systems.^[110] High conductivity and surface area are usually attributed to their enhanced performance.^[111] However, the role of CNT or graphene on bacterial metabolism is scarcely addressed. A recent study suggests that CNTs can alter the respiratory pathway of *Shewanella oneidensis* MR-1.^[112] Bacterial reduction of nitrobenzene (NB) is usually an intracellular process, but the addition of CNTs changed the intracellular reduction of NB to extracellular by promoting extracellular electron transfer (EET) pathway in *S. oneidensis* (**Figure 10A**). This finding reveals an unprecedented role of nanomaterials in bacterial respiration. Salvador et al.^[113] recently observed that CNTs can directly accelerate methanogens to produce methane by reducing redox potential (creating more negative redox potential). The enhancement in the methane production was directly proportional to CNT concentration and no methanogenic activity was observed in the absence of CNTs. This observation offers a novel strategy to accelerate hydrogenotrophic methane production from CO₂ at the cathode of MES by employing CNT networks (**Figure 5**). Modification of our Ni-based CCPHF cathodes with CNT resulted in 70% increase in acetate production rate from CO₂ in MES using a pure culture of the homoacetogenic bacterium *Sporomusa ovata*.^[114] A recent study showed that nanomaterials such as CNTs, TiO₂, SiO₂ and Al₂O₃ nanoparticles influence bacterial respiration and production of extracellular polymeric substances.^[115] Experimental and molecular dynamic simulation analyses demonstrated that CNT can enhance direct EET in *S. oneidensis* by developing a strong electronic conduit with OM c-Cyts (**Figure 10B**).^[116] Cell-secreted flavin mediated EET process is usually dominated in *S.*

oneidensis.^[117] Here, CNTs directly extract electrons from OM c-Cyts by promoting direct EET in *S. oneidensis*, which is energetically more favorable than mediated EET process. It is reasonable to predict that CNTs can facilitate bacterial electron uptake mechanisms as they function in the EET process.

Like CNTs, graphene also affects bacterial metabolism and response. A graphene bioanode stimulated the production of phenazine (cell-excreted mediator) in *Psuedomonas aeruginosa*-catalyzed MFC.^[118] The cell-excreted phenazine improved MFC performance by accelerating the EET process in *P. aeruginosa* like the role of flavin in *S. oneidensis*.^[117, 119] Magnetite nanoparticles^[120] and Au nanoparticles^[121] can act as substitutes for c-Cyts to lead EET processes in *Geobacter sulfurreducens* and *S. oneidensis*, respectively. These findings are extremely important as it is speculated that c-Cyts have a crucial role in electron uptake from the cathode.^[110, 122] Taken together, all these findings lead us to conclude that electrode material and surface properties play a major role in the metabolism and EET processes of microbes.

3.4. Possible Electron Transfer Mechanisms at the Bio-cathode and Conductive Materials that Facilitate Direct Electron Transfer

Much like artificial photosynthesis, MES draws inspiration from natural mechanisms; we can look to nature to aid in designing cathodes that mimic natural electron transfer processes for improved reaction kinetics. Direct biocorrosion is known to occur in sulfate-reducing bacteria in sedimentary environments, where they directly accept free electrons from a solid iron surface to circumvent rate-limiting dissociations and directly reduce protons to hydrogen.^[123] By observing this natural direct transfer/uptake mechanism, it is expected that some anaerobic

microorganisms can directly use electrodes as electron donors, which can be exploited within the context of MES.^[124] Two modes of electron transfer have been demonstrated: a) direct electron transfer and b) indirect electron transfer.^[125] Direct electron transfer encompasses the transfer of free electrons from the cathode to cells (**Figure 11A**), and between species through direct connections or electrically conductive materials (**Figure 11B**). The latter is referred to as direct interspecies electron transfer (DIET).^[125] Indirect, or mediated, electron transfer involves the electron movement between the cathode-cell and cell-cell interfaces via extracellular electron shuttles that can include molecular hydrogen and formate or excreted shuttles such as phenazine and riboflavin (**Figure 11C**).^[126, 127] Hydrogen evolves from the surface of many cathode materials through HER, while formate evolves as an organic oxidation intermediate or on cathode surfaces in the presence of CO₂ and protons as determined by the cathodic poised potential.^[124, 126]

Indirect electron transfer rates are highly dependent on mediator concentration gradients and are regulated by the energy available from catabolic reactions by the microorganisms.^[125, 128] The low solubility of H₂ and CO₂ directly affects their availability to microbial catalysts. For H₂, a high rate of evolution that is beyond the rate of microbial consumption (for example, methanogen H₂ half-saturation constant: 0.004 g H₂ /m³) in the biofilm would result in the escape of H₂, limiting its availability to the biofilm.^[16] This would not have a significant effect if direct electron transfer processes dominate at the bio-cathode, but it is worth considering when designing CCPHF cathodes where materials with exceptionally high HER capabilities may be unnecessary to pursue. Since direct electron transfer is independent of metabolite formation, it is favorable to promote in MES systems to eliminate undesired

side products, thus facilitating the stoichiometric conversion of CO₂ to value-added products.

[129]

While cathode-cell electron transfer is relevant at the interface of the biofilm attachment to the electrode, cell-cell electron transfer ^[130] is relevant as a mechanism for the entire thickness of the biofilm. Electron transfer rates can reach up to 40 × within the biofilm as compared to from electrodes to the biofilm.^[131] Since DIET is independent of mediator concentration gradients, there may be a substantial effect on reaction rates if DIET is a significant contributor to electron transfer, especially since thermodynamically it is more favorable compared to mediated transfer for long-range transport in biofilms.^[128] While DIET is mainly limited by redox cofactor activation losses,^[125, 128, 130, 132] it has been calculated to have a higher external electron transfer rate per cell pair (cp) compared to H₂-mediated electron transfer (44.9 × 10³ e⁻/cp/s vs. 5.24 × 10³ e⁻/cp/s, respectively).^[128] Cytochromes and pili are primary components in the DIET process^[125, 133, 134] ^[135] and they also play a role in direct cathode-cell electron transfer (**Figure 13A**). Cytochromes, key components in many metal-reducing bacteria, are membrane-associated heme proteins that transfer electrons during redox reactions.^[136] Pili are proteins that extend from the cell membrane; they are involved in cell adhesion, motility and DNA transfer, though in some cases they have exhibited conductive characteristics (from 37 μS cm⁻¹ – 188 mS cm⁻¹) which may be attributed to metallic-like conductivity^[137] or electron hopping via cytochromes located along the pili.^[138] **Table 2** outlines several co-cultured studies that demonstrate DIET between different microorganism pairs. Not only has direct solid-cell electron transfer been observed, but it has also been shown that cell-cell DIET is possible in microbial electrochemical systems, whether directly (i.e., cytochromes and pili) or via conductive materials (**Table 2**).

Studies investigating improved conversion rates and shorter start up lag times in anaerobic processes with the addition of conductive materials ^[139-142] ^[143] lay the groundwork for rational design of cathode material for CCPHF since conductive and semi-conductive materials are believed to serve as electrical conduits between species, even compensating for the lack of conductive membrane proteins (Table 2) as depicted in Figure 11B.^[144] These include carbon-based materials like CNTs^[141], carbon cloth^[145], carbon felt^[146], biochar^[145, 147], granular activated carbon (GAC)^[142, 148], graphite^[145, 146]; and metal-based materials like stainless steel^[143], haematite^[139], and magnetite.^[139, 140] These conductive materials can be used in the fabrication and decoration of CCPHF cathodes to facilitate the occurrence of DIET, for example by creating CNT forests on porous ceramic hollow fibers (Figure 5). An added advantage with CNT (or other nanoparticles) forests is increased surface roughness and porosity, thereby increasing the interfacial area of the cathode and the interactions at the cell-solid interface. This could ultimately lead to improved conversion rates as has been shown with Ni nanowire-network coated graphite cathodes.^[149] Such networks may also promote direct electron transfer by interacting with cytochrome heme groups, reducing the distance from the active site to the electrode for rapid electron transfer.^[150]

While the abovementioned materials are promising candidates to investigate and build on for an improved cathode design for CCPHF, it is important to understand how they interact with relevant microbial communities since these communities are complex and difficult to predict due to differences in species' physiology and diverse syntrophic relationships at the bio-cathode. ^[144] There is no single, generalized quantitative model for different electron transfer processes in mixed community microbial electrochemical systems. Specifically designed experiments are required to unequivocally determine the presence and contribution

of direct electron transfer within complex microbial communities, especially with the presence of HER at the cathode surface. Molecular genetic techniques and metatranscriptional data can be helpful in understanding the fundamentals of the processes by identifying unique gene expression patterns to distinguish between transfer mechanisms in specific microorganisms. Multi-omic data, coupled with modeling frameworks, are useful to understand the energetics of electron transfer, as well as the adaptive responses and dynamics of the interactions involved in the syntrophic growth of relevant cathodic microbial catalysts.^[128, 151] HER-incapable cathode materials such as indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) (**Figure 12**) can be used to simplify investigations by eliminating the possibility of an H₂-mediated pathway, only allowing for direct transfer routes throughout the biofilm. Such cathodes could also be applied in enrichment strategies that apply strong selective pressure for electroautotrophs that directly interact with solid electrodes as electron donors.

It is evident that rationally designed cathode materials for CCPHF are crucial in improving the performance of MES cells and the fundamental understanding of how microbial electrochemical systems function. Work with pure cultures has laid the groundwork for our understanding of electron transfer mechanisms in MES, but these conclusions are rarely realized in mixed community reactors as a systematic understanding is lacking. Ultimately, cathodic MES biofilms involve complex community dynamics, and a better understanding is envisioned to ultimately aid in the rational design of more efficient CCPHF cathodes for MES applications.

4. Conclusions and Perspectives

This progress report presents recent developments in dual-function macroporous hollow-fiber cathode architecture for converting waste streams, mainly wastewater and waste CO₂, to valuable resources using microbial electrochemical systems. The first part of the progress report presents and discusses the recent application of 3D CCPHF hierarchical cathode architecture as a new functional material for simultaneous recovery of clean freshwater and energy from wastewater in EMBR systems. The second part of the progress report also discusses the advantage of using CCPHF cathode architecture for MES applications to solve the issue of packing density for large-scale applications, increase the specific surface area of the cathode, avoid the gas-liquid mass transfer limitations that occur in other MES reactor configurations, and most importantly they are ideally suitable for on-site microbial electrochemical CCU of CO₂ gas generated from various industries.

Our early efforts for the development of polymer-based CCPHF cathodes^[35] have been very promising, and subsequent developments in this kind of functional material design may lead to a new generation of multifunctional CCPHF electrode materials for more efficient recovery of resources from wastewaters and recycling of CO₂ to value-added products. However, transforming polymeric hollow fiber membranes into CCPHF cathodes at large scale using ALD and other traditional coating methods is a challenge because of the intrinsic low chemical, thermal and mechanical stability of polymeric hollow fiber membranes. Alternatively, due to their high thermal, chemical and mechanical stability, ceramic hollow fiber membranes could be a suitable platform to fabricate CCPHF cathodes, using various surface modification techniques, including those that require harsh environments. Possible routes for transforming ceramic hollow fiber membranes into CCPHF cathodes were presented in this report. The surface of the ceramic-based CCPHF cathodes should perform

HER for EMBR application or be biocompatible for MES application. Even though Pt is the most active electrocatalyst for HER, its high cost and scarcity preclude its application at a large scale. Non-expensive, abundant and efficient metal catalysts for HER such as Ni, Co and Fe could be ideal for thin film catalyst deposition on ceramic hollow fiber membranes. Cost-effective 3D porous carbon-based materials such as CNT with easy synthesis route can further accelerate the efficiency of CCPHF cathodes for EMBR/MES systems. Further improvement in performance could be achieved by encapsulating CNTs with Ni, Co and Fe nanoparticles and their composite for high-efficiency HER. The use of composite materials combining HER metal catalyst and carbon-based material are advantageous for enhancing the microbial electrochemical CCU in MES by increasing biocompatibility and electrical conductivity.

Improving the availability of CO₂ from the atmosphere and combustion gases to microbial catalysts is an important aspect to consider for the commercial application of CCPHF cathodes in MES. Integrating CO₂-adsorbing materials such as water stable molecular sieves (e.g., zeolites) and MOFs with CCPHF cathodes can promote the CO₂ conversion by providing sufficient CO₂ for the bacterial conversion. In this regard, Cu-based MOFs are promising candidates for the design of CCPHF cathodes for MES application.

In MES, the interactions taking place at the abiotic-biotic interface are the driving force for all the relevant product-forming reactions. Therefore, knowledge on how electrode topography and material can affect the physiology of microbial catalysts, and the electron transfer mechanisms occurring at the abiotic-biotic interface will be useful for the rational design of high-performing cathodes for MES. In this progress report we presented the possible electron transfer mechanisms (direct and indirect) that could take place at the bio-

cathode and discussed the role of certain carbon- and metal-based materials in enhancing DIET between microbial species. The role of these materials in enhancing direct electron transfer in MES systems is yet to be determined

Hybrid systems, inspired by natural photosynthesis, combining inorganic and microbial components to convert CO₂ to value-added products are recently gaining attention in the scientific community.^[70, 71, 152] The development of photocathodes in MES systems is a sustainable approach to produce solar biofuels from CO₂. Solar energy is the most abundant source of renewable energy, and when solar light is used to drive the MES process, it represents an alternative form of natural photosynthesis. A recent classical study has already demonstrated that the photo-active semiconductor based-solar-hybrid MES system could exceed the efficiency of natural photosynthesis.^[70] Further advances in the cathode material and architecture could significantly improve the efficiency of MES for converting solar energy to value-added chemicals into a range where large-scale applications become possible.

Acknowledgements

This work was supported by Center Competitive Funding Program (FCC/1/1971-05-01) and Competitive Research Grant (URF/1/2985-01-01) from King Abdullah University of Science and Technology (KAUST). Figures were created by Xavier Pita (Figures 2, 7 and 12), Ivan Gromicho (Figures 5, 8 and ToC image) and Heno Hwang (Figures 4 and ToC image), scientific illustrators at KAUST. We thank Srikanth Pedireddy, a Postdoctoral Fellow in the WDRC at KAUST, for modifying Figure 3 and generating Figures 1 and 6 in this manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] J. Machell, K. Prior, R. Allan, J. M. Andresen, *Environ Sci-Wat Res* 2015, 1, 15.
- [2] C. M. Sales, P. K. H. Lee, *Curr Opin Biotech* 2015, 33, 260; M. C. M. van Loosdrecht, D. Brdjanovic, *Science* 2014, 344, 1452.
- [3] D. Puyol, D. Batstone, T. Hulsen, S. Astals, M. Peces, J. O. Kromer, *Front Microbiol* 2017, 7.
- [4] K. P. Katuri, C. M. Werner, R. J. Jimenez-Sandoval, W. Chen, S. Jeon, B. E. Logan, Z. P. Lai, G. L. Army, P. E. Saikaly, *Environmental Science & Technology* 2014, 48, 12833.
- [5] M. Jinxing, W. Zhiwei, M. Bin, Z. Junyao, W. Zhichao, *Current Environmental Engineering* 2015, 2, 38; E. S. Heidrich, J. Dolfing, K. Scott, S. R. Edwards, C. Jones, T. P. Curtis, *Appl Microbiol Biot* 2013, 97, 6979; I. Ieropoulos, J. Greenman, C. Melhuish, *Physical Chemistry Chemical Physics* 2012, 14, 94; P. T. Kelly, Z. He, *Bioresource Technol* 2014, 153, 351; P. Ledezma, P. Kuntke, C. J. N. Buisman, J. Keller, S. Freguia, *Trends Biotechnol* 2015, 33, 214; M. R. Arredondo, P. Kuntke, A. W. Jeremiasse, T. H. J. A. Sleutels, C. J. N. Buisman, A. ter Heijne, *Environ Sci-Wat Res* 2015, 1, 22.
- [6] U. S. D. o. Energy, <https://scripps.ucsd.edu/programs/keelingcurve/> 2017.
- [7] E. Union, https://ec.europa.eu/clima/policies/strategies/progress/monitoring_en 2017.
- [8] S. P. Cuellar-Bermudez, J. S. Garcia-Perez, B. E. Rittmann, R. Parra-Saldivar, *J Clean Prod* 2015, 98, 53.
- [9] L. Garcia-Gonzalez, M. S. I. Mozumder, M. Dubreuil, E. I. P. Volcke, H. De Wever, *Catal Today* 2015, 257, 237.
- [10] X. Dominguez-Benetton, S. Sandipam, Y. Satyawali, K. Vanbroekhoven, D. Pant, *Journal of Microbial & Biochemical Technology* 2013, S6, 1; Y. A.-G. Sandipam Srikanth, Karolien Vanbroekhoven, Deepak Pant, *ChemPhysChem* 2017, 18, 1.
- [11] K. P. Nevin, T. L. Woodard, A. E. Franks, Z. M. Summers, D. R. Lovley, *Mbio* 2010, 1.
- [12] S. Bajracharya, S. Srikanth, G. Mohanakrishna, R. Zacharia, D. P. B. T. B. Strik, D. Pant, *J Power Sources* 2017, 356, 256.
- [13] S. Bajracharya, M. Sharma, G. Mohanakrishna, X. D. Benneton, D. P. B. T. B. Strik, P. M. Sarma, D. Pant, *Renew Energ* 2016, 98, 153.
- [14] N. Aryal, F. Ammam, S. A. Patil, D. Pant, *Green Chemistry* 2017.
- [15] J. C. Wei, P. Liang, X. Huang, *Bioresource Technol* 2011, 102, 9335; M. H. Zhou, M. L. Chi, J. M. Luo, H. H. He, T. Jin, *J Power Sources* 2011, 196, 4427; K. Guo, A. PrevotEAU, S. A. Patil, K. Rabaey, *Curr Opin Biotech* 2015, 33, 149; S. Kerzenmacher, Springer Berlin Heidelberg, Berlin, Heidelberg, 1; J. M. Sonawane, A. Yadav, P. C. Ghosh, S. B. Adeloju,

- Biosens Bioelectron 2017, 90, 558; S. Kalathil, S. A. Patil, D. Pant, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier, 2017.
- [16] C. M. Werner, K. P. Katuri, A. R. Hari, W. Chen, Z. P. Lai, B. E. Logan, G. L. Amy, P. E. Saikaly, *Environmental Science & Technology* 2016, 50, 4439.
- [17] J. Li, Z. Ge, Z. He, *Bioresource Technol* 2014, 167, 310; J. Li, Z. Ge, Z. He, *J Chem Technol Biot* 2014, 89, 1330; L. J. Ren, Y. Ahn, B. E. Logan, *Environmental Science & Technology* 2014, 48, 4199; J. Wang, Y. W. Zheng, H. Jia, H. W. Zhang, *Bioresource Technol* 2013, 149, 163; J. Wang, Y. W. Zheng, H. Jia, H. W. Zhang, *Bioresource Technol* 2014, 170, 483; Y. P. Wang, X. W. Liu, W. W. Li, F. Li, Y. K. Wang, G. P. Sheng, R. J. Zeng, H. Q. Yu, *Appl Energ* 2012, 98, 230; Z. Ge, Q. Y. Ping, Z. He, *J Chem Technol Biot* 2013, 88, 1584.
- [18] L. H. Huang, X. F. Li, Y. P. Ren, X. H. Wang, *Rsc Adv* 2017, 7, 20824.
- [19] Y. K. Wang, G. P. Sheng, W. W. Li, Y. X. Huang, Y. Y. Yu, R. J. Zeng, H. Q. Yu, *Environmental Science & Technology* 2011, 45, 9256.
- [20] J. Song, L. F. Liu, F. L. Yang, N. Q. Ren, J. Crittenden, *Bioresource Technol* 2013, 147, 409.
- [21] J. D. Liu, L. F. Liu, B. Gao, F. L. Yang, *J Membrane Sci* 2013, 430, 196.
- [22] L. Malaeb, K. P. Katuri, B. E. Logan, H. Maab, S. P. Nunes, P. E. Saikaly, *Environmental Science & Technology* 2013, 47, 11821.
- [23] Z. W. Wang, J. Huang, C. W. Zhu, J. X. Ma, Z. C. Wu, *Chem Eng Technol* 2013, 36, 2044.
- [24] Y. J. Li, L. F. Liu, J. D. Liu, F. L. Yang, N. Q. Ren, *Desalination* 2014, 349, 94.
- [25] G. Y. Zhang, H. M. Zhang, Y. J. Ma, G. G. Yuan, F. L. Yang, R. Zhang, *Enzyme Microb Tech* 2014, 60, 56.
- [26] J. D. Liu, L. F. Liu, B. Gao, F. L. Yang, J. Crittenden, N. Q. Ren, *Int J Hydrogen Energ* 2014, 39, 17865.
- [27] K. C. Zuo, S. Liang, P. Liang, X. C. Zhou, D. Y. Sun, X. Y. Zhang, X. Huang, *Bioresource Technol* 2015, 185, 426.
- [28] Y. H. Li, L. F. Liu, F. L. Yang, N. Q. Ren, *J Membrane Sci* 2015, 484, 27.
- [29] K. C. Zuo, H. Liu, Q. Y. Zhang, P. Liang, C. D. Vecitis, X. Huang, *Electrochim Acta* 2016, 211, 199.
- [30] P. Zhang, Y. P. Qu, J. Liu, Y. J. Feng, *Rsc Adv* 2016, 6, 4587.
- [31] I. Merino-Jimenez, C. Santoro, S. Rojas-Carbonell, J. Greenman, I. Ieropoulos, P. Atanassov, *Catalysts* 2016, 6, 127.
- [32] M. Kodali, C. Santoro, A. Serov, S. Kabir, K. Artyushkova, I. Matanovic, P. Atanassov, *Electrochim Acta* 2017, 231, 115; V. J. Watson, C. N. Delgado, B. E. Logan, *Environmental Science & Technology* 2013, 47, 6704.
- [33] R. C. Huang, W. J. Chiu, I. P. J. Lai, C. C. Huang, *Sci Rep-Uk* 2015, 5; L. Xu, G. Q. Zhang, G. E. Yuan, H. Y. Liu, J. D. Liu, F. L. Yang, *Rsc Adv* 2015, 5, 22533.
- [34] C. Hanson, in *Biomass Magazine*, 2014; T. H. J. A. Sleutels, A. Ter Heijne, C. J. N. Buisman, H. V. M. Hamelers, *Chemsuschem* 2012, 5, 1012.
- [35] K. P. Katuri, N. M. S. Bettahalli, X. B. Wang, G. Matar, S. Chisca, S. P. Nunes, P. E. Saikaly, *Adv Mater* 2016, 28, 9504.
- [36] R. Kas, K. K. Hummadi, R. Kortlever, P. de Wit, A. Milbrat, M. W. J. Luiten-Olieman, N. E. Benes, M. T. M. Koper, G. Mul, *Nat Commun* 2016, 7.

- [37] M. Wang, L. Chen, L. Sun, *Energy Environ. Sci.* 2012, 5, 6763.
- [38] I. Roger, M. A. Shipman, M. D. Symes, *Nat Rev Chem* 2017, 1.
- [39] Y. Ito, W. T. Cong, T. Fujita, Z. Tang, M. W. Chen, *Angew Chem Int Edit* 2015, 54, 2131.
- [40] E. P. Patrizia Formoso, Giovanni De Filpo, Fiore Pasquale Nicoletta, *Membranes* 2017, 7.
- [41] J. Huang, Z. W. Wang, J. Y. Zhang, X. R. Zhang, J. X. Ma, Z. C. Wu, *Sci Rep-Uk* 2015, 5; W. Y. Duan, A. Ronen, S. Walker, D. Jassby, *Acs Appl Mater Inter* 2016, 8, 22574; A. V. Dudchenko, J. Rolf, K. Russell, W. Y. Duan, D. Jassby, *J Membrane Sci* 2014, 468, 1; A. Ronen, W. Y. Duan, I. Wheeldon, S. Walker, D. Jassby, *Environmental Science & Technology* 2015, 49, 12741; C. F. de Lannoy, D. Jassby, K. Gloe, A. D. Gordon, M. R. Wiesner, *Environmental Science & Technology* 2013, 47, 2760; Q. Liu, G. L. Qiu, Z. Z. Zhou, J. G. Li, G. L. Amy, J. P. Xie, J. Y. Lee, *Environmental Science & Technology* 2016, 50, 10596.
- [42] F. Ahmed, B. S. Lalia, V. Kochkodan, N. Hilal, R. Hashaikeh, *Desalination* 2016, 391, 1.
- [43] M. A. Abdulhameed, M. H. D. Othman, A. F. Ismail, T. Matsuura, Z. Harun, M. A. Rahman, M. H. Puteh, J. Jaafar, M. Rezaei, S. K. Hubadillah, *J Clean Prod* 2017, 140, 1731.
- [44] M. Tavakkoli, T. Kallio, O. Reynaud, A. G. Nasibulin, C. Johans, J. Sainio, H. Jiang, E. I. Kauppinen, K. Laasonen, *Angew Chem Int Edit* 2015, 54, 4535; E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis, R. E. Schaak, *J Am Chem Soc* 2013, 135, 9267; M. Gong, W. Zhou, M. C. Tsai, J. G. Zhou, M. Y. Guan, M. C. Lin, B. Zhang, Y. F. Hu, D. Y. Wang, J. Yang, S. J. Pennycook, B. J. Hwang, H. J. Dai, *Nat Commun* 2014, 5; S. Losse, J. G. Vos, S. Rau, *Coordin Chem Rev* 2010, 254, 2492.
- [45] J. Chae, H. S. Park, S. W. Kang, *Electrochem Solid St* 2002, 5, C64.
- [46] A. P. Espejo, R. Zierold, J. Gooth, J. Dendooven, C. Detavernier, J. Escrig, K. Nielsch, *Nanotechnology* 2016, 27.
- [47] T. D. Gould, A. M. Lubers, B. T. Neltner, J. V. Carrier, A. W. Weimer, J. L. Falconer, J. W. Medlin, *J Catal* 2013, 303, 9.
- [48] E. Makino, M. Uenoyama, T. Shibata, *Sensor Actuat a-Phys* 1998, 71, 187.
- [49] V. Martynov, A. D. Johnson, V. Gupta, *J Phys Iv* 2003, 112, 845.
- [50] H. Y. Noh, K. H. Lee, X. X. Cui, C. S. Choi, *Scripta Mater* 2000, 43, 847.
- [51] A. Agarwal, M. Pujari, R. Uppaluri, A. Verma, *Ceram Int* 2014, 40, 691.
- [52] A. Heidarzadeh, R. T. Mousavian, R. A. Khosroshahi, Y. A. Afkham, H. Pouraliakbar, *Rare Metals* 2017, 36, 209.
- [53] C. X. Cai, J. Chen, *Anal Biochem* 2004, 332, 75.
- [54] S. Mazumder, N. Sarkar, J. G. Park, I. J. Kim, *Mater Lett* 2015, 161, 212; S. Mazumder, N. Sarkar, J. G. Park, W. Zhao, S. Kim, I. J. Kim, *Chem Phys Lett* 2015, 635, 334.
- [55] A. V. Dudchenko, C. Chen, A. Cardenas, J. Rolf, D. Jassby, *Nat Nanotechnol* 2017, 12, 557.
- [56] X. F. Fan, H. M. Zhao, X. Quan, Y. M. Liu, S. Chen, *Water Res* 2016, 88, 285.
- [57] D. Y. Wang, M. Gong, H. L. Chou, C. J. Pan, H. A. Chen, Y. P. Wu, M. C. Lin, M. Y. Guan, J. Yang, C. W. Chen, Y. L. Wang, B. J. Hwang, C. C. Chen, H. J. Dai, *J Am Chem Soc* 2015, 137, 1587.

- [58] W. Wang, W. Chu, N. Wang, W. Yang, C. F. Jiang, *Int J Hydrogen Energ* 2016, 41, 967.
- [59] X. Y. Lu, W. L. Yim, B. H. R. Suryanto, C. Zhao, *J Am Chem Soc* 2015, 137, 2901; B. H. R. Suryanto, S. Chen, J. J. Duan, C. Zhao, *Acs Appl Mater Inter* 2016, 8, 35513.
- [60] X. X. Zou, X. X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova, T. Asefa, *Angew Chem Int Edit* 2014, 53, 4372; J. Deng, P. J. Ren, D. H. Deng, L. Yu, F. Yang, X. H. Bao, *Energ Environ Sci* 2014, 7, 1919.
- [61] Q. Liu, J. Q. Tian, W. Cui, P. Jiang, N. Y. Cheng, A. M. Asiri, X. P. Sun, *Angew Chem Int Edit* 2014, 53, 6710.
- [62] Y. Pan, W. H. Hu, D. P. Liu, Y. Q. Liu, C. G. Liu, *J Mater Chem A* 2015, 3, 13087.
- [63] M. N. Young, M. J. Links, S. C. Papat, B. E. Rittmann, C. I. Torres, *Chemsuschem* 2016, 9, 3345.
- [64] N. Li, J. K. An, L. A. Zhou, T. Li, J. H. Li, C. J. Feng, X. Wang, *J Power Sources* 2016, 306, 495.
- [65] J. Barber, P. D. Tran, *J R Soc Interface* 2013, 10; J. Barber, B. Andersson, *Nature* 1994, 370, 31.
- [66] B. Barstow, *Advanced Science, Engineering and Medicine* 2015, 7, 1066.
- [67] Y. Kim, J. H. Lee, H. Ha, S. W. Im, K. T. Nam, *Nano Converg* 2016, 3, 19.
- [68] O. Adesina, I. A. Anzai, J. L. Avalos, B. Barstow, *Chem* 2017, 2, 20.
- [69] K. K. Sakimoto, N. Kornienko, P. Yang, *Accounts Chem Res* 2017, 50, 476; J. P. Torella, C. J. Gagliardi, J. S. Chen, D. K. Bediako, B. Colon, J. C. Way, P. A. Silver, D. G. Nocera, *P Natl Acad Sci USA* 2015, 112, 2337; C. Liu, J. J. Gallagher, K. K. Sakimoto, E. M. Nichols, C. J. Chang, M. C. Y. Chang, P. D. Yang, *Nano Lett* 2015, 15, 3634; V. Muller, *Science* 2016, 351, 34.
- [70] C. Liu, B. C. Colon, M. Ziesack, P. A. Silver, D. G. Nocera, *Science* 2016, 352, 1210.
- [71] E. M. Nichols, J. J. Gallagher, C. Liu, Y. D. Su, J. Resasco, Y. Yu, Y. J. Sun, P. D. Yang, M. C. Y. Chang, C. J. Chang, *P Natl Acad Sci USA* 2015, 112, 11461.
- [72] K. K. Sakimoto, A. B. Wong, P. D. Yang, *Science* 2016, 351, 74.
- [73] L. Jourdin, S. Freguia, B. C. Donose, J. Chen, G. G. Wallace, J. Keller, V. Flexer, *J Mater Chem A* 2014, 2, 13093.
- [74] Q. Fu, Y. Kuramochi, N. Fukushima, H. Maeda, K. Sato, H. Kobayashi, *Environmental Science & Technology* 2015, 49, 1225.
- [75] M. Alqahtani, V. Sapireddy, K. Katuri, Y. Yu, Z. Lai, P. Saikaly, *A Novel Electrically Conductive and Porous Hollow Fiber Cathode design for Recycling CO₂ to CH₄ through Electromethanogenesis. Book of abstracts: The 3rd european meeting of the international society for microbial electrochemistry and technology (EU-ISMET 2016)*, F. Aulenta, & M. Majone, Rome 2016.
- [76] V. Mortezaeikia, O. Tavakoli, R. Yegani, M. Faramarzi, *Greenh Gases* 2016, 6, 218.
- [77] L. Jourdin, Y. Lu, V. Flexer, J. Keller, S. Freguia, *Chemelectrochem* 2016, 3, 581.
- [78] T. Zhang, H. R. Nie, T. S. Bain, H. Y. Lu, M. M. Cui, O. L. Snoeyenbos-West, A. E. Franks, K. P. Nevin, T. P. Russell, D. R. Lovley, *Energ Environ Sci* 2013, 6, 217.
- [79] M. Cui, H. Nie, T. Zhang, D. Lovley, T. P. Russell, *Sustainable Energy Fuels* 2017.
- [80] T. Krieg, A. Sydow, U. Schroder, J. Schrader, D. Holtmann, *Trends Biotechnol* 2014, 32, 645.
- [81] J. Hou, Z. Liu, S. Yang, Y. Zhou, *J Power Sources* 2014, 258, 204.

- [82] Y. F. Fan, F. Rezaei, Y. Labreche, R. P. Lively, W. J. Koros, C. W. Jones, *Fuel* 2015, 160, 153.
- [83] F. Akhtar, L. Andersson, S. Ogunwumi, N. Hedin, L. Bergstrom, *J Eur Ceram Soc* 2014, 34, 1643.
- [84] R. W. Baker, B. T. Low, *Macromolecules* 2014, 47, 6999.
- [85] M. Hugler, S. M. Sievert, *Annu Rev Mar Sci* 2011, 3, 261; L. Li, M. L. Fu, Y. H. Zhao, Y. T. Zhu, *Environ Sci Pollut R* 2012, 19, 4227.
- [86] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chem Rev* 2012, 112, 724.
- [87] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, *Accounts Chem Res* 2010, 43, 58.
- [88] R. S. Bedi, D. E. Beving, L. P. Zanello, Y. S. Yan, *Acta Biomater* 2009, 5, 3265; Y. P. Guo, T. Long, Z. F. Song, Z. A. Zhu, *J Biomed Mater Res B* 2014, 102, 583.
- [89] X. Y. Wu, F. Tong, T. S. Song, X. Y. Gao, J. J. Xie, C. C. Zhou, L. X. Zhang, P. Wei, *J Chem Technol Biot* 2015, 90, 87.
- [90] X. Y. Wu, F. Tong, X. Y. Yong, J. Zhou, L. X. Zhang, H. H. Jia, P. Wei, *J Hazard Mater* 2016, 308, 303.
- [91] P. N. Venkatesan, S. Dharmalingam, *Rsc Adv* 2015, 5, 84004.
- [92] C. Wang, Z. G. Xie, K. E. deKrafft, W. L. Lin, *J Am Chem Soc* 2011, 133, 13445; P. Z. Li, X. J. Wang, J. Liu, J. S. Lim, R. Q. Zou, Y. L. Zhao, *J Am Chem Soc* 2016, 138, 2142.
- [93] S. J. You, X. B. Gong, W. Wang, D. P. Qi, X. H. Wang, X. D. Chen, N. Q. Ren, *Adv Energy Mater* 2016, 6.
- [94] H. L. Tang, S. C. Cai, S. L. Xie, Z. B. Wang, Y. X. Tong, M. Pan, X. H. Lu, *Adv Sci* 2016, 3.
- [95] N. C. Burtch, H. Jasuja, K. S. Walton, *Chem Rev* 2014, 114, 10575.
- [96] A. J. Howarth, T. C. Wang, S. S. Al-Juaid, S. G. Aziz, J. T. Hupp, O. K. Farha, *Dalton T* 2016, 45, 93.
- [97] A. J. Brown, N. A. Brunelli, K. Eum, F. Rashidi, J. R. Johnson, W. J. Koros, C. W. Jones, S. Nair, *Science* 2014, 345, 72.
- [98] J. Albo, D. Vallejo, G. Beobide, O. Castillo, P. Castano, A. Irabien, *Chemsuschem* 2017, 10, 1100.
- [99] I. Choi, Y. E. Jung, S. J. Yoo, J. Y. Kim, H. J. Kim, C. Y. Lee, J. H. Jang, *J Electrochem Sci Te* 2017, 8, 61.
- [100] R. Hinogami, S. Yotsuhashi, M. Deguchi, Y. Zenitani, H. Hashiba, Y. Yamada, *Ecs Electrochem Lett* 2012, 1, H17.
- [101] I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha, J. T. Hupp, *Acs Catal* 2015, 5, 6302.
- [102] A. Corma, H. Garcia, *J Catal* 2013, 308, 168; A. Mahmood, W. H. Guo, H. Tabassum, R. Q. Zou, *Adv Energy Mater* 2016, 6.
- [103] K. Anselme, P. Davidson, A. Popa, M. Giazxon, M. Liley, L. Ploux, *Acta Biomater* 2010, 6, 3824.
- [104] F. J. H. Hol, C. Dekker, *Science* 2014, 346, 438; A. Susarrey-Arce, I. Sorzabal-Bellido, A. Oknianska, F. McBride, A. J. Beckett, J. G. E. Gardeniers, R. Raval, R. M. Tiggelaar, Y. A. D. Fernandez, *J Mater Chem B* 2016, 4, 3104.

- [105] L. Rizzello, B. Sorce, S. Sabella, G. Vecchio, A. Galeone, V. Brunetti, R. Cingolani, P. P. Pompa, *Acs Nano* 2011, 5, 1865.
- [106] R. Helbig, D. Gunther, J. Friedrichs, F. Rossler, A. Lasagni, C. Werner, *Biomater Sci-Uk* 2016, 4, 1074.
- [107] L. C. Hsu, J. Fang, D. A. Borca-Tasciuc, R. W. Worobo, C. I. Moraru, *Appl Environ Microb* 2013, 79, 2703.
- [108] R. J. Crawford, H. K. Webb, V. K. Truong, J. Hasan, E. P. Ivanova, *Adv Colloid Interfac* 2012, 179, 142; K. Bohinc, G. Drazic, R. Fink, M. Oder, M. Jevsnik, D. Nipic, K. Godic-Torkar, P. Raspor, *Int J Adhes Adhes* 2014, 50, 265.
- [109] H. E. Jeong, I. Kim, P. Karam, H. J. Choi, P. D. Yang, *Nano Lett* 2013, 13, 2864.
- [110] S. Kalathil, D. Pant, *Rsc Adv* 2016, 6, 30582.
- [111] A. ElMekawy, H. M. Hegab, D. Losic, C. P. Saint, D. Pant, *Renew Sust Energ Rev* 2017, 72, 1389.
- [112] F. F. Yan, Y. R. He, C. Wu, Y. Y. Cheng, W. W. Li, H. Q. Yu, *Environ Sci Tech Let* 2014, 1, 128.
- [113] A. F. Salvador, G. Martins, M. Melle-Franco, R. Serpa, A. J. Stams, A. J. Cavaleiro, M. A. Pereira, M. M. Alves, *Environ Microbiol* 2017.
- [114] B. Bian, M. F. Alqahtani, K. P. Katuri, D. Liu, Z. Lai, P. Saikaly, *Rational Design of Cathode Materials for Microbial Electrosynthesis. Book of abstracts: General Meeting of the International Society for Microbial Electrochemistry and Technology (Lisbon 2017)*, ISMET, Lisbon 2017.
- [115] T. Ergon-Can, D. Y. Koseoglu-Imer, O. F. Algur, I. Koyuncu, *Clean-Soil Air Water* 2016, 44, 1508.
- [116] X. W. Liu, J. J. Chen, Y. X. Huang, X. F. Sun, G. P. Sheng, D. B. Li, L. Xiong, Y. Y. Zhang, F. Zhao, H. Q. Yu, *Sci Rep-Uk* 2014, 4.
- [117] E. Marsili, D. B. Baron, I. D. Shikhare, D. Coursolle, J. A. Gralnick, D. R. Bond, *P Natl Acad Sci USA* 2008, 105, 3968.
- [118] J. Liu, Y. Qiao, C. X. Guo, S. Lim, H. Song, C. M. Li, *Bioresource Technol* 2012, 114, 275.
- [119] S. Kalathil, K. Hashimoto, A. Okamoto, *Chemelectrochem* 2014, 1, 1840.
- [120] F. Liu, A. E. Rotaru, P. M. Shrestha, N. S. Malvankar, K. P. Nevin, D. R. Lovley, *Environ Microbiol* 2015, 17, 648.
- [121] R. R. Wu, L. Cui, L. X. Chen, C. Wang, C. L. Cao, G. P. Sheng, H. Q. Yu, F. Zhao, *Sci Rep-Uk* 2013, 3.
- [122] D. E. Ross, J. M. Flynn, D. B. Baron, J. A. Gralnick, D. R. Bond, *Plos One* 2011, 6.
- [123] H. T. Dinh, J. Kuever, M. Mußmann, A. W. Hassel, M. Stratmann, F. Widdel, *Nature* 2004, 427, 829.
- [124] J. S. Deutzmann, M. Sahin, A. M. Spormann, *Mbio* 2015, 6.
- [125] Q. Cheng, D. F. Call, *Environmental Science: Processes & Impacts* 2016, 18, 968.
- [126] M. C. A. A. van Eerten-Jansen, N. C. Jansen, C. M. Plugge, V. de Wilde, C. J. N. Buisman, A. ter Heijne, *J Chem Technol Biot* 2015, 90, 963; P.-L. Tremblay, L. T. Angenent, T. Zhang, *Trends Biotechnol* 2016.
- [127] D. R. Lovley, *Annual review of microbiology* 2012, 66, 391; M. Rosenbaum, F. Aulenta, M. Villano, L. T. Angenent, *Bioresource Technol* 2011, 102, 324.
- [128] T. Storck, B. Viridis, D. J. Batstone, *Isme J* 2016, 10, 621.

- [129] J. M. Flynn, D. E. Ross, K. A. Hunt, D. R. Bond, J. A. Gralnick, *Mbio* 2010, 1.
- [130] Z. M. Summers, H. E. Fogarty, C. Leang, A. E. Franks, N. S. Malvankar, D. R. Lovley, *Science* 2010, 330, 1413.
- [131] H. K. Ly, F. Harnisch, S. F. Hong, U. Schroder, P. Hildebrandt, D. Millo, *Chemsuschem* 2013, 6, 487.
- [132] A. Kouzuma, S. Kato, K. Watanabe, *Front Microbiol* 2015, 6, 477.
- [133] M. Y. El-Naggar, G. Wanger, K. M. Leung, T. D. Yuzvinsky, G. Southam, J. Yang, W. M. Lau, K. H. Neelson, Y. A. Gorby, *Proceedings of the National Academy of Sciences* 2010, 107, 18127.
- [134] A.-E. Rotaru, P. M. Shrestha, F. Liu, B. Markovaite, S. Chen, K. P. Nevin, D. R. Lovley, *Appl Environ Microb* 2014, 80, 4599.
- [135] F. H. Liu, A. E. Rotaru, P. M. Shrestha, N. S. Malvankar, K. P. Nevin, D. R. Lovley, *Environ Microbiol* 2015, 17, 648; S. Kato, K. Hashimoto, K. Watanabe, *Proceedings of the National Academy of Sciences* 2012, 109, 10042; L. P. Nielsen, N. Risgaard-Petersen, H. Fossing, P. B. Christensen, M. Sayama, *Nature* 2010, 463, 1071.
- [136] X. Qian, T. Mester, L. Morgado, T. Arakawa, M. L. Sharma, K. Inoue, C. Joseph, C. A. Salgueiro, M. J. Maroney, D. R. Lovley, *Biochimica et Biophysica Acta (BBA)-Bioenergetics* 2011, 1807, 404.
- [137] D. R. Lovley, Portland Press Limited, 2012.
- [138] D. R. Bond, S. M. Strycharz-Glaven, L. M. Tender, C. I. Torres, *Chemsuschem* 2012, 5, 1099.
- [139] S. Kato, K. Hashimoto, K. Watanabe, *Environ Microbiol* 2012, 14, 1646.
- [140] C. Cruz Viggi, S. Rossetti, S. Fazi, P. Paiano, M. Majone, F. Aulenta, *Environmental science & technology* 2014, 48, 7536.
- [141] L.-L. Li, Z.-H. Tong, C.-Y. Fang, J. Chu, H.-Q. Yu, *Water Res* 2015, 70, 1.
- [142] Y. Yang, Y. Zhang, Z. Li, Z. Zhao, X. Quan, Z. Zhao, *J Clean Prod* 2017, 149, 1101.
- [143] Y. Li, Y. Zhang, Y. Yang, X. Quan, Z. Zhao, *Bioresource Technol* 2017, 234, 303.
- [144] D. R. Lovley, *Isme J* 2017, 11, 327.
- [145] Z. Zhao, Y. Zhang, T. Woodard, K. Nevin, D. Lovley, *Bioresource Technol* 2015, 191, 140.
- [146] Z. Zhao, Y. Zhang, X. Quan, H. Zhao, *Bioresource Technol* 2016, 200, 235.
- [147] S. Chen, A.-E. Rotaru, P. M. Shrestha, N. S. Malvankar, F. Liu, W. Fan, K. P. Nevin, D. R. Lovley, *Sci Rep-Uk* 2014, 4, 5019.
- [148] N. LaBarge, Y. D. Yilmazel, P.-Y. Hong, B. E. Logan, *Bioelectrochemistry* 2017, 113, 20.
- [149] H. R. Nie, T. Zhang, M. M. Cui, H. Y. Lu, D. R. Lovley, T. P. Russell, *Physical Chemistry Chemical Physics* 2013, 15, 14290.
- [150] M. Khairy, S. A. El-Safty, *Chem Commun* 2014, 50, 1356.
- [151] H. Nagarajan, M. Embree, A. E. Rotaru, P. M. Shrestha, A. M. Feist, B. O. Palsson, D. R. Lovley, K. Zengler, *Nat Commun* 2013, 4.
- [152] T. Zhang, *Science* 2015, 350, 738.
- [153] S. Chen, A.-E. Rotaru, F. Liu, J. Philips, T. L. Woodard, K. P. Nevin, D. R. Lovley, *Bioresource Technol* 2014, 173, 82.
- [154] F. Liu, A.-E. Rotaru, P. M. Shrestha, N. S. Malvankar, K. P. Nevin, D. R. Lovley, *Energy Environ Sci* 2012, 5, 8982.

- [155] A.-E. Rotaru, P. M. Shrestha, F. Liu, M. Shrestha, D. Shrestha, M. Embree, K. Zengler, C. Wardman, K. P. Nevin, D. R. Lovley, *Energy Environ Sci* 2014, 7, 408.
- [156] S. Hattori, H. Luo, H. Shoun, Y. Kamagata, *Journal of bioscience and bioengineering* 2001, 91, 294.

Table 1. Microfiltration and ultrafiltration flat sheet cathodes in microbial fuel cells.

Electrically conductive membrane	Pore size	Membrane area	Substrate support where applicable	Fabrication approach	Ref.
Stainless steel (SS) mesh	40 μm	494 cm^2	-	NA	[19]
SS mesh	Not provided	75 cm^2	-	NA	[20]
Polypyrrole (PPy) polymerized polyester filter cloth	Not provided	800 cm^2	Polyester filter cloth	Vapor phase polymerization	[21]
Multiwalled carbon nanotubes (MWCNTs) membrane	0.065 μm	7 cm^2	Polyester nonwoven membrane (pore size 40 μm)	Dispersing MWCNTs as a multilayer on porous membrane through vacuum filtration	[22]
SS mesh	48 μm	32 cm^2	-	NA	[23]
PPy modified SS membrane	Not provided	27 cm^2	SS mesh	Electro-polymerization	[24]
SS mesh	13 μm	30 cm^2	-	NA	[25]
SS mesh	15 μm	800 cm^2	-	NA	[26]

Carbon membrane	0.5 μm	7 cm^2	Carboxymethyl cellulose binder	Membrane casting in mould followed by pressing at 25 MPa	[27]
Carbon fiber cathode membrane with catalyst	Not provided	Not available	Carbon fiber cloth	Casting solution (Polyvinylidene fluoride (PVDF) and catalyst) dispersed on the carbon fiber cloth followed by phase inversion	[28]
Nitrogen doped carbon nanotube (CNT) membrane	Not provided	7 cm^2	Polytetrafluoroethylene (PTFE) membrane (pore size 5 μm)	Dispersing MWCNTs and N-CNT on porous membrane through vacuum filtration	[29]
Carbon and SS composite membrane	Not provided	7 cm^2	SS mesh	Carbon layer casted on SS mesh through rolling-press method	[30]
Reduce graphene oxide (RGO)-carbon membrane	0.09 μm	7 cm^2	SS mesh and polypropylene non-woven base	Immersion-precipitation phase transformation: PVDF solution containing RGO casted on a SS mesh and polypropylene nonwoven base using a coating machine	[18]

Dashes “-” are used to indicate that there is no substrate support (Column 4). NA: not available (Column 5).

Table 2. Co-cultured studies investigating DIET with CO₂ or HCO₃⁻ as electron acceptor.

Co-cultured organisms	Conductive material	Electron donor	Electron acceptor	Aggregates	DIET reported?	Ref.
<i>G. metallireducens</i> & <i>Methanosarcina barkeri</i> DSM 800	Carbon cloth	10 mM ethanol	CO ₂ or HCO ₃ ⁻	No	Yes, accelerated metabolism with carbon cloth	[153]
<i>G. metallireducens</i> & <i>M. barkeri</i> DSM 800	GAC ^a	20 mM ethanol	CO ₂ or HCO ₃ ⁻	No	Yes, accelerated metabolism with GAC	[154]
<i>G. metallireducens</i> (wild type, Δ <i>pilA</i>) & <i>Methanosaeta harundinacea</i> JCM-13211	-	20 mM ethanol	CO ₂ or HCO ₃ ⁻	Yes	Yes, but only with wild type	[155]
<i>G. metallireducens</i> (wild type, Δ <i>pilA</i>) & <i>Methanospirillum hungatei</i> DSM-13809	-	20 mM ethanol	CO ₂ or HCO ₃ ⁻	-	No	[155]
<i>G. metallireducens</i> (wild type, Δ <i>pilA</i>) & <i>Methanobacterium formicicum</i> DSM-1535	-	20 mM ethanol	CO ₂ or HCO ₃ ⁻	-	No	[155]
<i>G. metallireducens</i> (ATCC 53744 wild type, Δ <i>pilA</i> or c-type cytochrome Δ <i>Gmet</i> _1868) & <i>M. barkeri</i> DSM 800	GAC	20 mM ethanol	CO ₂ or HCO ₃ ⁻	Yes	Yes, rescue activity by GAC for Δ <i>pilA</i> and Δ <i>Gmet</i> _1868 GAC also reduces lag time to convert ethanol in wild type	[134]
<i>M. barkeri</i> DSM 800 & <i>P. carbinolicus</i> DSM 2380	-	20 mM ethanol	CO ₂ or HCO ₃ ⁻	No	No	[134]

<i>G. metallireducens</i> GS-15 & <i>M. barkeri</i> DSM 800	Biochar	20 mM ethanol	CO ₂ or HCO ₃ ⁻	No	Yes, only in presence of biochar	[147]
<i>Thermacetogenium phaeum</i> PB & <i>Methanothermobacter thermautotrophicus</i> TM	-	40 mM acetate	HCO ₃ ⁻	-	No, only via HIT/FIT ^b	[156]
<i>T. phaeum</i> PB & <i>M. thermautotrophicus</i> ΔH	-	40 mM acetate	HCO ₃ ⁻	-	No, only via HIT	[156]
<i>Methanobacterium formicicum</i> (DSM 1535T)	MWCNT 0.1, 0.5, 1.0 and 5.0 g/L	2 mM acetate	H ₂ /CO ₂	-	Yes, enhanced rates and faster start up with CNTs	[113]
<i>Methanospirillum hungatei</i> (DSM 864T)	MWCNT 0.1, 0.5, 1.0 and 5.0 g/L	2 mM acetate	H ₂ /CO ₂	-	Yes, enhanced rates and faster start up with CNTs	[113]
<i>Methanosaeta concilii</i> (DSM 3671T)	MWCNT 0.1, 0.5, 1.0 and 5.0 g/L	10 mM acetate	CO ₂	-	Yes, slight enhanced rates and faster start up with CNTs up to 1g/L	[113]
<i>Methanosarcina mazei</i> (DSM 2053T)	MWCNT 0.1, 0.5, 1.0 and 5.0 g/L	20 mM acetate	CO ₂	Yes	Yes, slight enhanced rates and faster start up with CNTs up to 1g/L	[113]
<i>M. hungatei</i> (DSM 864T) & <i>Syntrophomonas wolfei</i> (DSM 102351T)	MWCNT 0.1, 0.5, 1.0 and 5.0 g/L	20 mM butyrate	CO ₂	-	Perhaps, HIT more significant	[113]

^aGAC: granular activated carbon; ^bHIT: hydrogen involved transfer; FIT: formate involved transfer

Dashes “-” are used to indicate: no addition of conductive material (Column 2); no mention of aggregation (Column 5)

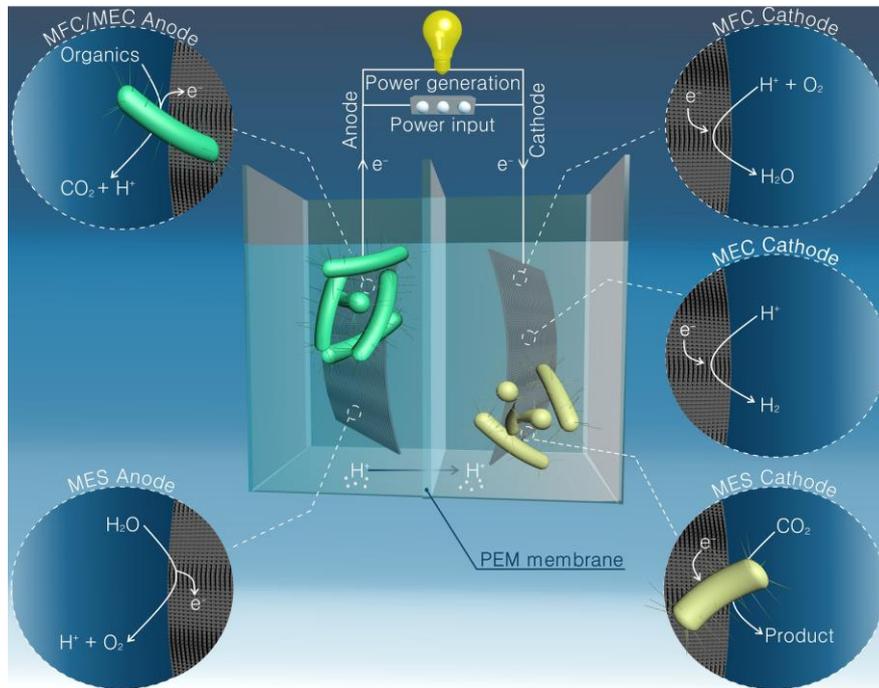


Figure 1. A cartoon representation of the different applications of microbial electrochemical systems for converting waste streams (wastewater and CO_2) to valuable resources. MFC: microbial fuel cell; MEC: microbial electrolysis cell; MES: microbial electrosynthesis; PEM: proton exchange membrane.

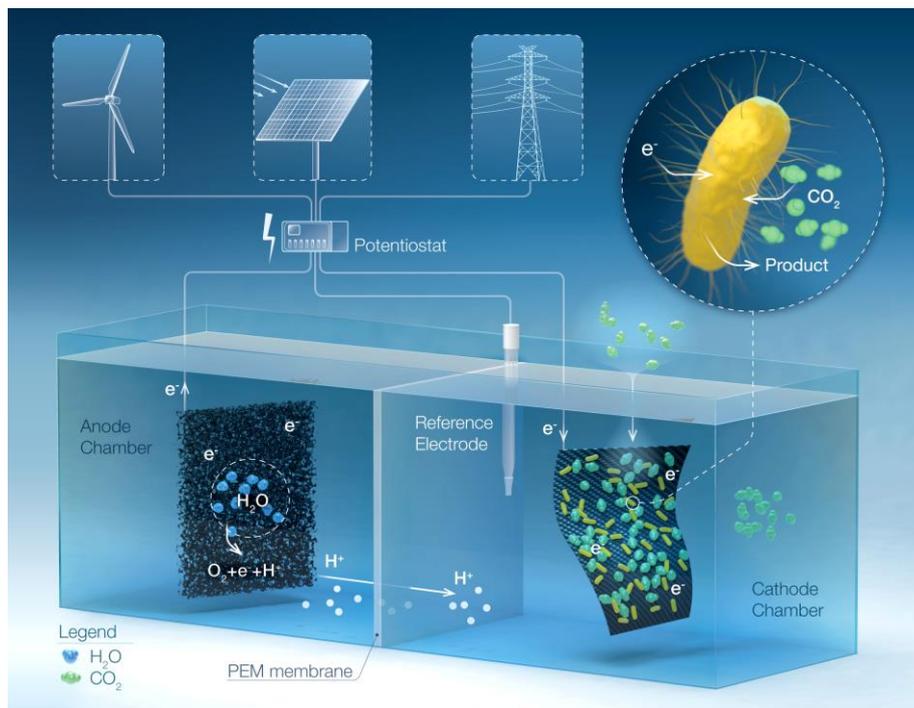


Figure 2. Schematic of a microbial electrosynthesis (MES) cell powered with different energy sources (wind, solar or electrical grid). PEM: proton-exchange membrane.

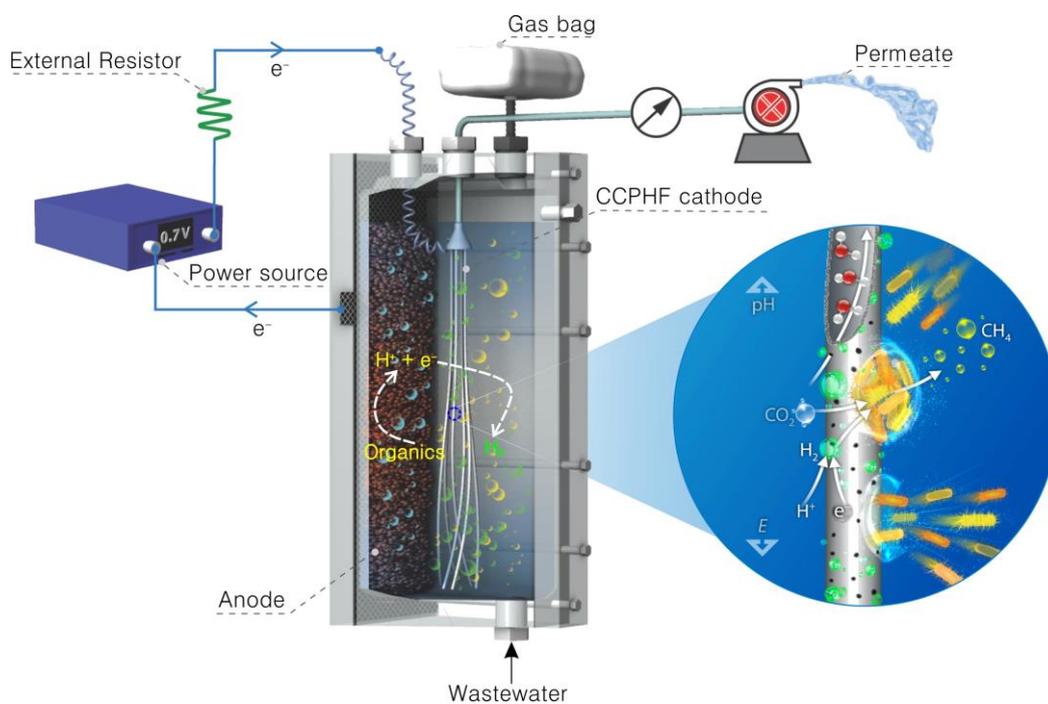


Figure 3. Schematic of the electrochemical membrane bioreactor (EMBR). The electrically conductive, catalytic and porous hollow fiber (CCPHF) cathode contains microfiltration pores that allow water to pass through while blocking the passage of bacteria. In addition to its role as a filter, the CCPHF cathode catalyzes the hydrogen evolution reaction (HER) at the cathode surface. The hydrogen generated at the cathode surface can be utilized by hydrogenotrophic methanogens to generate methane gas. Reproduced with permission.^[4, 16] Copyright 2014 and 2016, American Chemical Society.

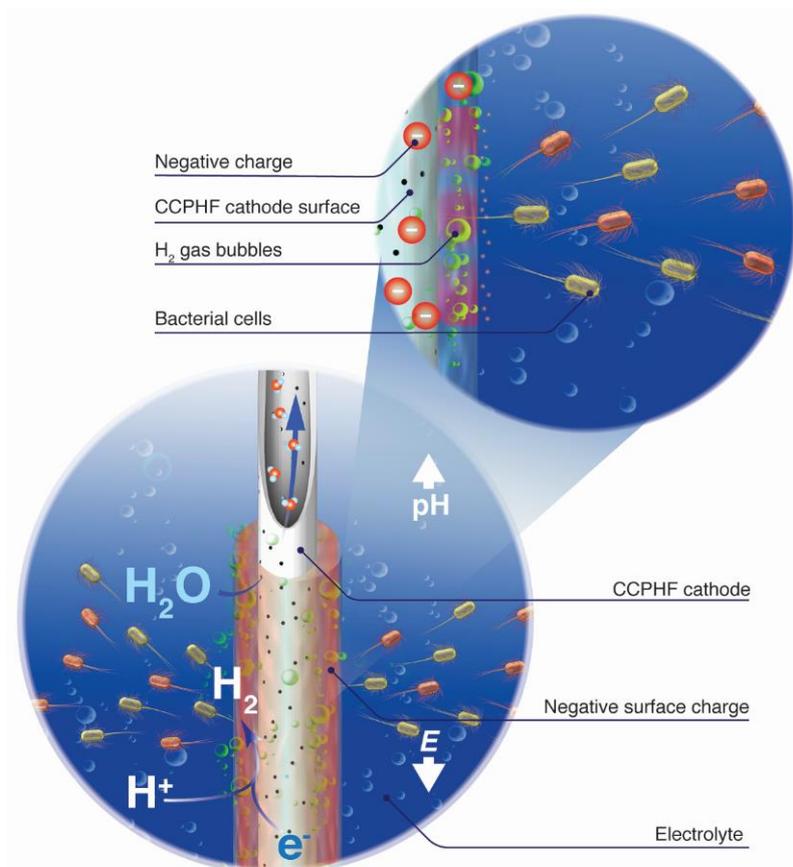


Figure 4. A cartoon representation of biofouling mitigation mechanisms in the electrochemical membrane bioreactor (EMBR). CCPHF: electrically conductive, catalytic and porous hollow fiber.

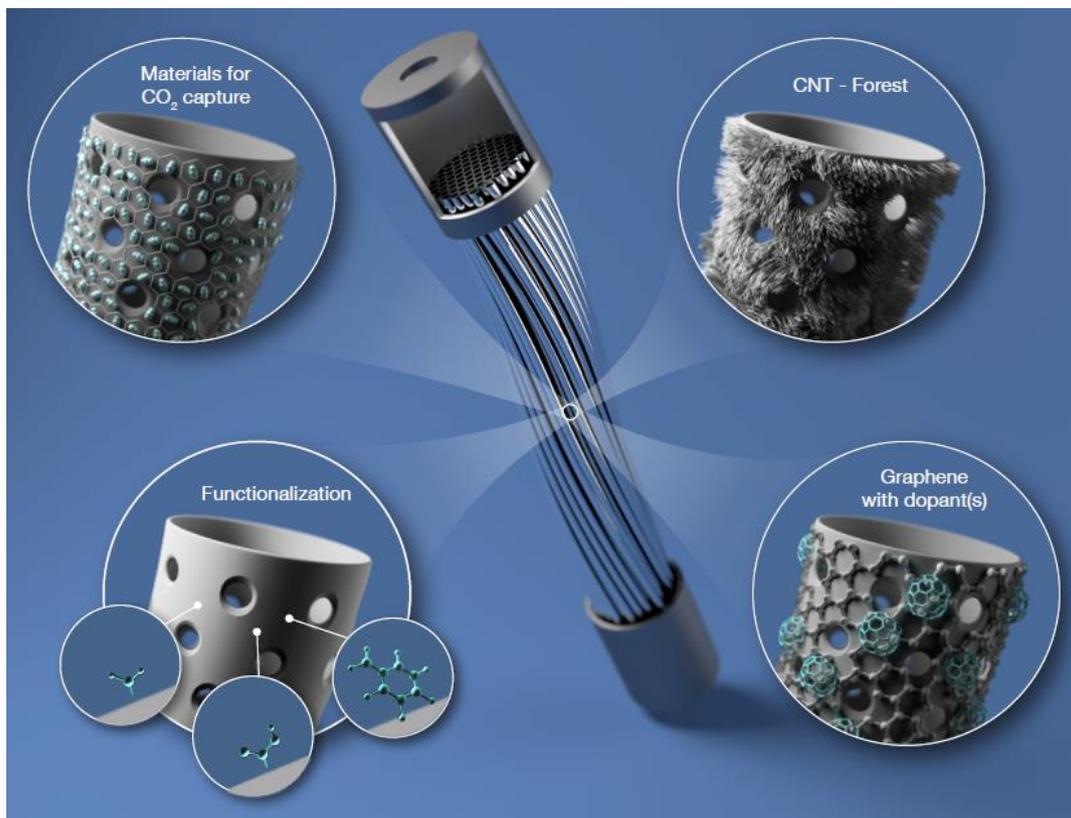


Figure 5. Schematic illustration showing possible surface modifications on porous hollow fiber membranes. CNT: carbon nanotube.

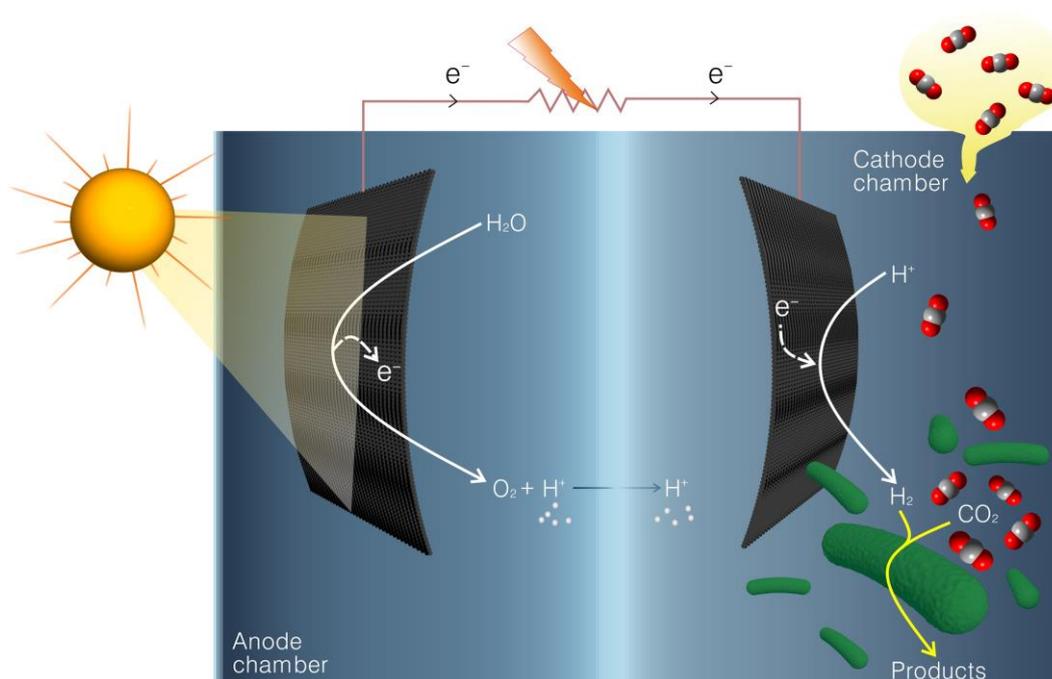


Figure 6. Schematic representation of coupling solar light with microorganisms to reduce CO_2 to high-value chemicals.

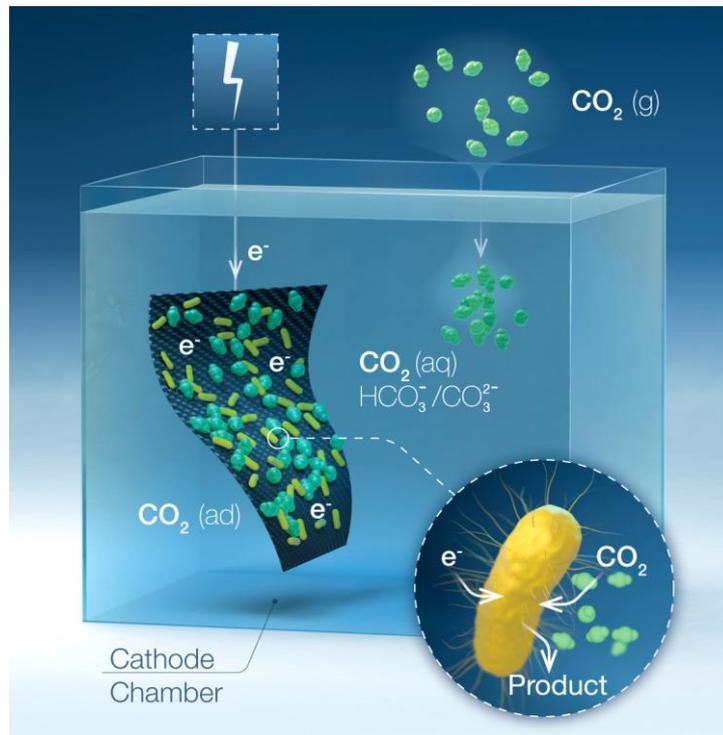


Figure 7. Cartoon representation of electroautotrophs fixing different forms of CO_2 .

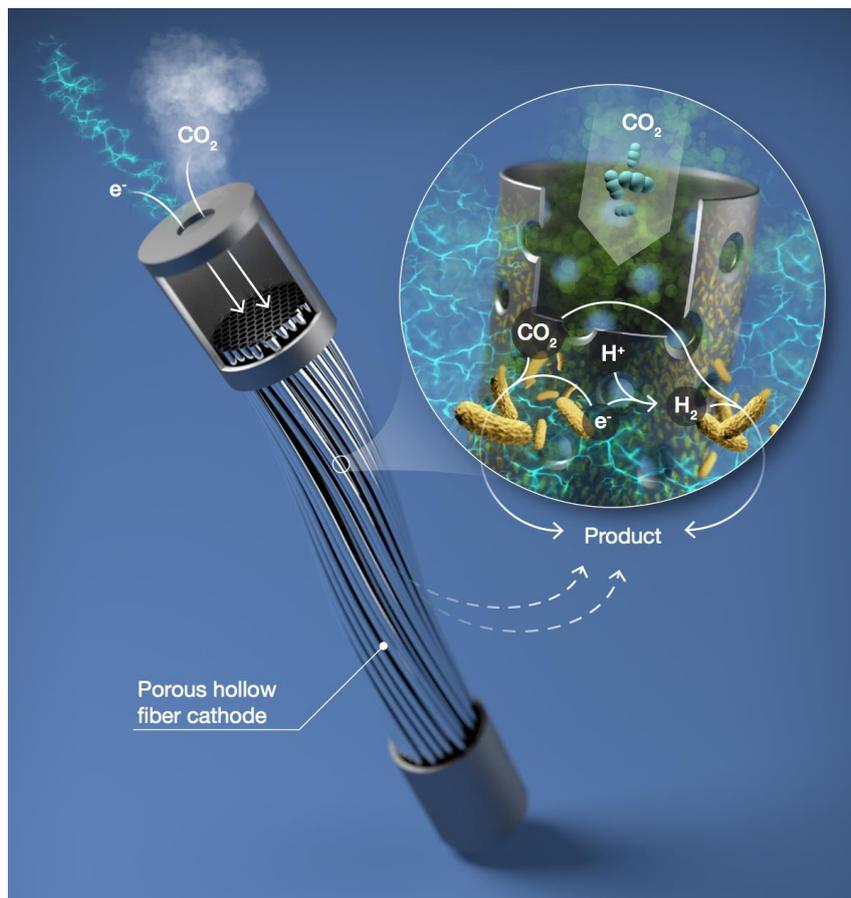


Figure 8. Schematic of electrically conductive, catalytic and porous hollow fiber (CCPHF) cathode with dual functions: cathode for hydrogen evolution reaction (HER) and for direct delivery of CO_2 gas to electroautotrophs through the pores in the hollow fibers.

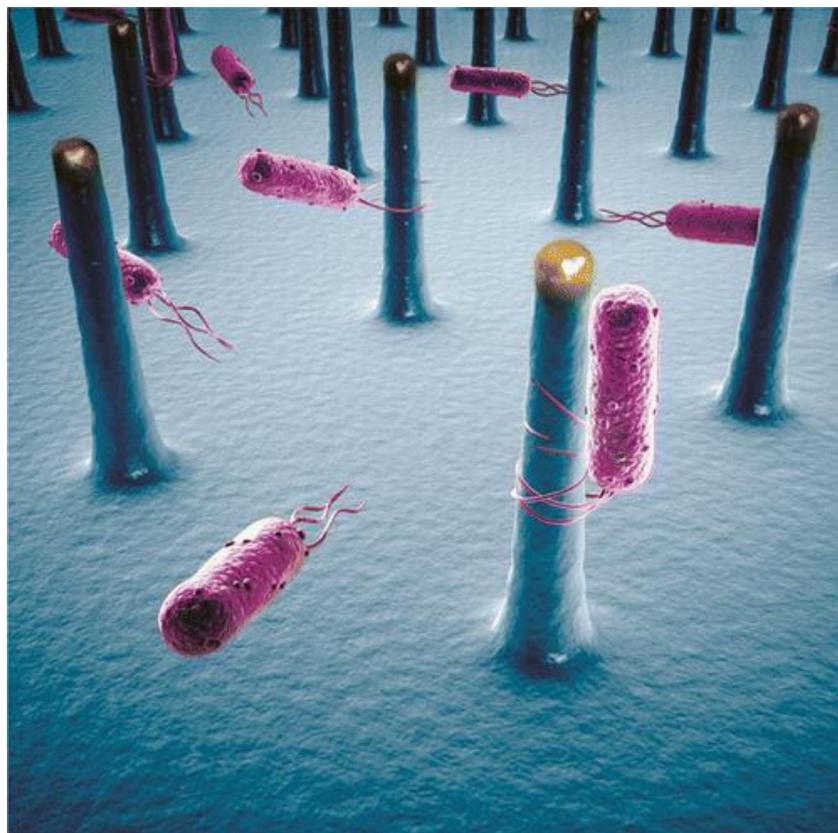


Figure 9. Shows bacterial sensing of nano-topography. Bacterial cells are attached to silicon (Si) nanowires instead of sitting on the planar Si substrate by sensing nanotopography. Reproduced with permission.^[109] Copyright 2013, American Chemical Society.

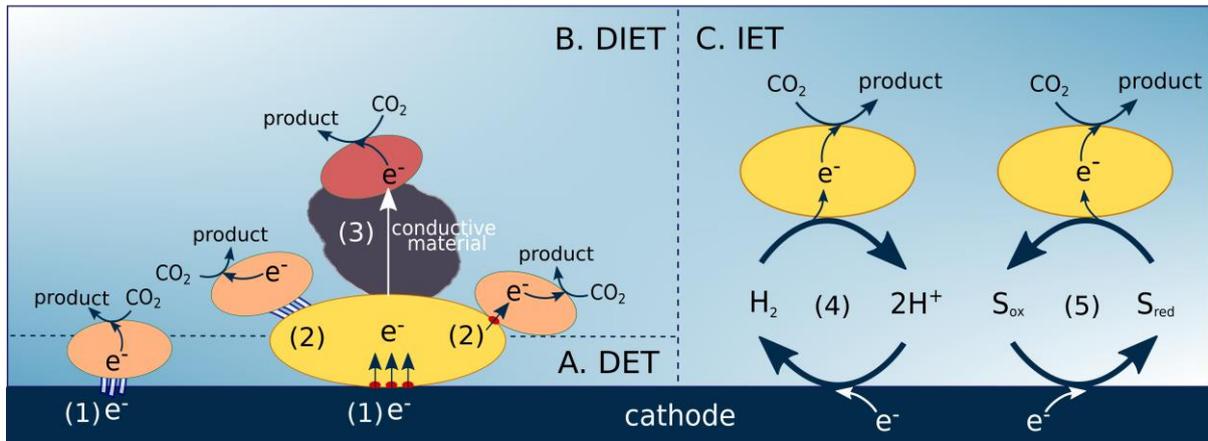


Figure 11. Schematic diagram of electron transfer at the cathode via (A) Direct electron transfer (DET), (B) Direct interspecies electron transfer (DIET), and (C) Indirect electron transfer (IET). The different electron transfer pathways shown are (1) DET from the cathode to the microbial catalyst via cytochromes, or conductive nanowires, (2) DIET via cytochromes or conductive nanowires, (3) DIET between different microbial catalyst species via a conductive material, (4) IET via an exogenous electron shuttle (H_2 -mediated in this case) and (5) IET via shuttles excreted from the microbial catalyst (e.g., phenazine and flavins).

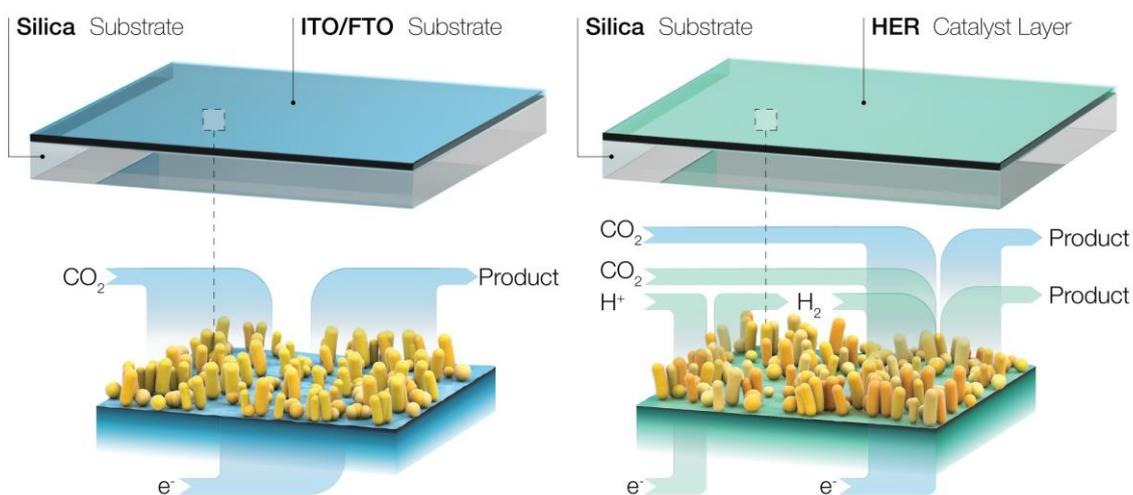


Figure 12. A schematic representation of cathodes coated with either an ITO/FTO layer, which only allows for direct electron transfer from the cathode to electroautotrophs for CO_2 reduction to value-added products, or a HER catalyst layer, where both direct (blue arrows) or H_2 -mediated electron transfer (green arrows) can take place. ITO: indium tin oxide; FTO: fluorine doped tin oxide; HER: hydrogen evolution reaction.

Electro-catalytic and macroporous hollow fiber cathode for converting waste streams (e.g., wastewater and CO₂) to valuable resources (clean water, energy and value-added products).

Keywords: microbial electrosynthesis, electrochemical membrane bioreactor, CO₂ reduction, electrically conductive membrane, artificial photosynthesis

K. P. Katuri, S. Kalathil, A. Ragab, B. Bian, M. F. Alqahtani, D. Pant, and P. E. Saikaly*

Dual-Function Electro-Catalytic and Macroporous Hollow-Fiber Cathode for Converting Waste Streams to Valuable Resources Using Microbial Electrochemical Systems

