

## Perspective

## Electrosynthesis, modulation, and self-driven electroseparation in microbial fuel cells

Iwona Gajda,<sup>1</sup> Jiseon You,<sup>1</sup> Buddhi Arjuna Mendis,<sup>1</sup> John Greenman,<sup>1</sup> and Ioannis A. Ieropoulos<sup>1,\*</sup>

## SUMMARY

**Microbial electrosynthesis (MES) represents a sustainable platform that converts waste into resources, using microorganisms within an electrochemical cell. Traditionally, MES refers to the oxidation/reduction of a reactant at the electrode surface with externally applied potential bias. However, microbial fuel cells (MFCs) generate electrons that can drive electrochemical reactions at otherwise unbiased electrodes. Electrosynthesis in MFCs is driven by microbial oxidation of organic matter releasing electrons that force the migration of cationic species to the cathode. Here, we explore how electrosynthesis can coexist within electricity-producing MFCs thanks to electro-separation of cations, electroosmotic drag, and oxygen reduction within appropriately designed systems. More importantly, we report on a novel method of *in situ* modulation for electrosynthesis, through additional “pin” electrodes. Several MFC electrosynthesis modulating methods that adjust the electrode potential of each half-cell through the pin electrodes are presented. The innovative concept of electrosynthesis within the electricity producing MFCs provides a multidisciplinary platform converting waste-to-resources in a self-sustainable way.**

## ELECTROSYNTHESIS IN MICROBIAL FUEL CELLS

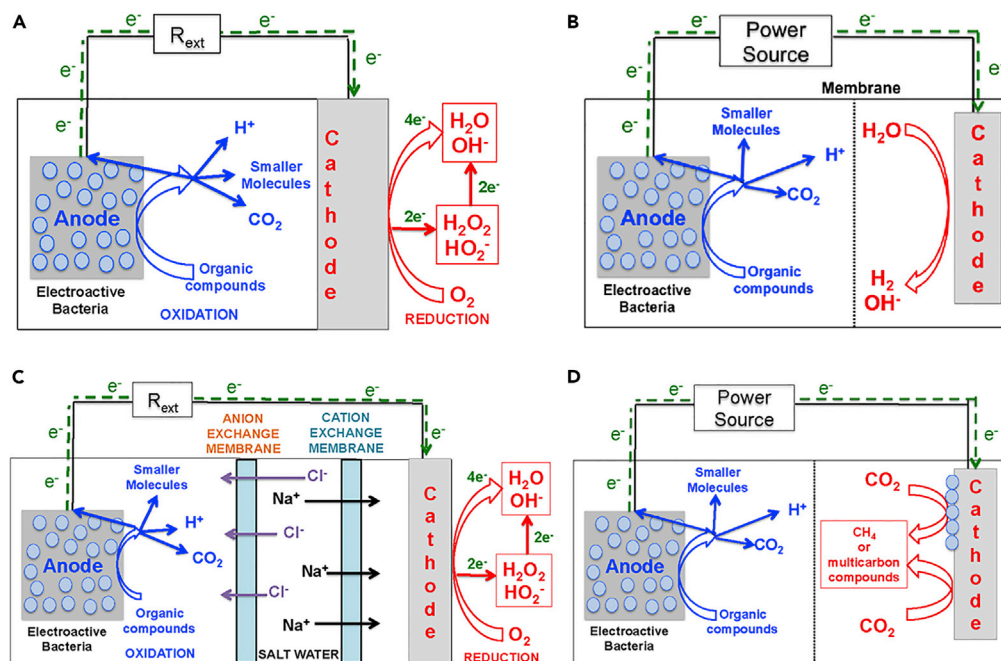
Growing industrialization, alongside accelerated resource consumption put natural resources under significant strain, globally; there is therefore a clear need for new, green and sustainable solutions. An ever-increasing research interest on bio-based economy looks into the use of wastewater for the extraction of energy from organic carbon, pollutant removal, chemical synthesis, and resource recovery. The development of new technologies in the area of bioelectrochemistry looks at the interactions between microbes and electrodes to explore the possibility of sustainable transformation of various types of waste (organics, pollutants and CO<sub>2</sub>) into value-added products through green chemistry. The role of microorganisms incorporates the use of renewable electricity for CO<sub>2</sub> recycling and commodity production (Bian et al., 2020), while the metal-microbe interface enables the microbes to capture energy directly from sunlight, which is then used for sustainable biosynthesis of chemicals (Sahoo et al., 2020). In the past decade, more emphasis has been given on producing high-value products and chemicals from waste streams, moving toward a circular economy and sustainable production. Compared with conventional chemical-based electrosynthesis, bioelectrochemical system (BES)-driven electrosynthesis can eliminate or reduce the use of high value commodities such as redox reagents, noble materials and/or toxic or hazardous substances. Reactions generally take place at (or close to) ambient temperature and pressure. Therefore BES-based electrosynthesis can also be utilized to produce different industrial commodities sustainably by replacing existing chemical-based production streams.

The variety of configurations and extensive research in BES have resulted in the development of several research paths including: microbial fuel cell (MFC) for electricity generation (Chen et al., 2019); microbial electrolysis cell (MEC) for the production of biofuels such as hydrogen and methane (Wang and Ren, 2013); microbial electrosynthesis (MES) for the production of value-added products (Jiang and Jianxiang Zeng, 2018); and microbial desalination cell (MDC) for salt removal and desalination (Saeed et al., 2015). Although many different configurations and cell architectures are possible for these BESs, the initial examples, mainly MFCs, were adapted from hydrogen fuel cells, where an ion exchange membrane is sandwiched between the anode and cathode. However, unlike the hydrogen fuel cells where relatively fast reactions occur under high temperature and pressure, BESs have different design requirements. Therefore, new cell architectures have been developed to achieve performance enhancement, sustainability, and

<sup>1</sup>Bristol BioEnergy Centre, Bristol Robotics Laboratory, T-Block, Frenchay Campus, University of the West of England (UWE Bristol), Bristol BS16 1QY, UK

\*Correspondence: ioannis.ieropoulos@bri.ac.uk  
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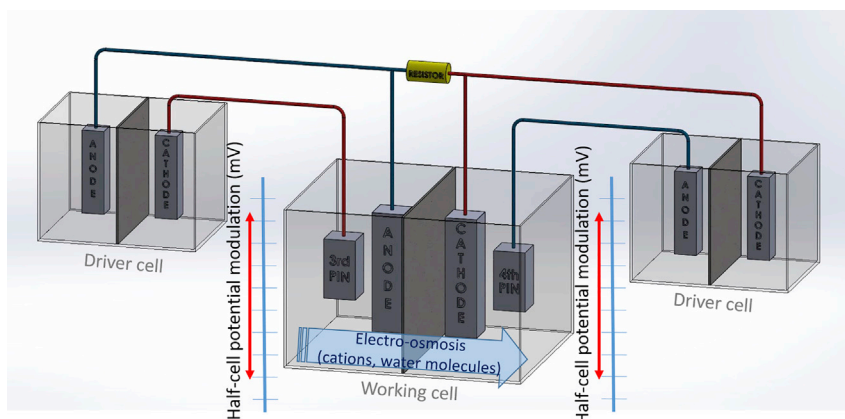
**Figure 1. BES system schematics**

Scheme of operating principles of microbial fuel cell (A), microbial electrolysis cell (B), microbial desalination cell (C), and general microbial electrosynthesis cell (D). Adapted from (Santoro et al., 2017).

cost-effectiveness. The operating principles of each BES system in a typical design are depicted in Figure 1. Electron transfer is a fundamental part of the biological and chemical redox reactions responsible for the conversions of elements in the natural environment. On a BES platform, the microbial extracellular electron transfer can assist by either producing electrons in the anodic reactions or consuming electrons in the cathodic reactions.

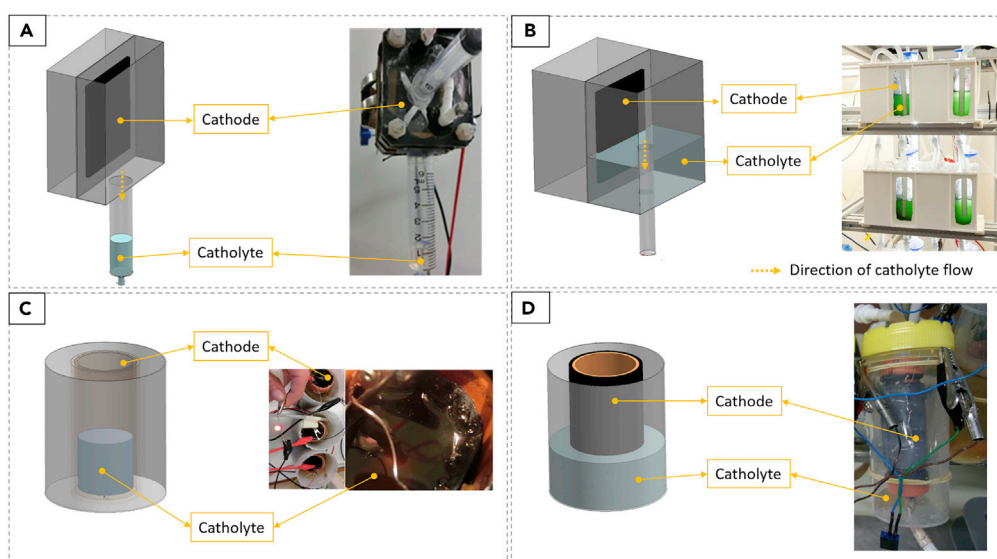
Electrosynthesis is defined as the synthesis of chemical compounds in an electrochemical cell, which could achieve higher selectivity as well as yields, in comparison with ordinary redox reactions (Leech et al., 2020; Pletcher, 2018). For example, MES exploits microbes for synthesis reactions as shown in Figure 1D. Research into microbial electrochemistry and interactions between living microbial cells and electrodes gave rise to the new area of bioelectrochemistry, growing from fundamental studies that gained interest from researchers and engineers into new technology that is aiming to transform waste products into resources (Schröder et al., 2015; Zou and He, 2018). From the electrosynthesis standpoint, two approaches focus on either microbial (MES) or chemical (MEC) catalysis, whereas both use the biological contingent, and the difference is the biological or chemical uptake (reduction) on the cathode that determines the final products. Both processes use an external power source to drive the transformations (Figures 1B and 1D); however the emphasis on the future development of self-powered catalysis should be directed to MFC and MDC configurations that are able to generate electrical output thanks to microbial oxidation (electroactive bacteria, Figure 1). In this perspective, some initial research avenues are investigated to understand how self-sustainable electrosynthesis could be integrated within a truly unique BES architecture to become both energy efficient and entirely self-driven.

As already mentioned, the main research focus of MFCs has been electricity generation whilst treating organic waste both in liquid and solid forms. More recently, however, researchers started paying attention to its potential for electrosynthesis (Dong et al., 2018; Gajda et al., 2015; Wang and Ren, 2014). In MFCs, electrons generated through microbial oxidation force the electroseparation of cationic species from the anode to the cathode. The migration of cationic species from the anode to the cathode does not have to be an undesired condition to overcome but a distinctive advantage of the MFC operation and is fundamental in self-driven process resulting in pH and ion separation. A recent study emphasizes how pH splitting and  $H^+/OH^-$  migration can be exploited to integrate the electrosynthesis, separation,



**Figure 2. Multifunctional MFC with additional pin electrodes as a way to control electrosynthesis**

concentration, and recovery in bioelectrochemical reactions (Zeppilli et al., 2021). Thanks to the possibility of continuously generating acidity or alkalinity in different MFC compartments and ability to regulate it via an electrical circuit, specific bioelectrochemical processes can be controlled (Zeppilli et al., 2021) for target environmental applications (Pikaar et al., 2019). In MFCs, the electrosynthesis of catholyte is a self-driven energy-positive process that is a product of ion separation, electroosmotic drag and oxygen reduction reaction (ORR) resulting in the extraction of valuable by-products in the cathode (Figures 1 and 3). The use of a bioanode in combination with a chemical cathode was already presented for electrosynthesis of caustic compounds (Rabaey and Rozendal, 2010) or hydrogen peroxide (Rozendal et al., 2009) utilizing both ion migration, as well as ORR functionality. Electrosynthesis of target products depends on several process parameters such as the microbiome, feedstock composition and concentration, pH, temperature, and electrode potential, as well as on bioreactor design and constituent components such as electrocatalysts and membranes (Kong et al., 2020). External potential levels that need to be applied on working electrodes depend on the oxidation/reduction process occurring at the half-cell. This mechanism is mainly determined by the type of metabolic pathway, applied potential, and the nature of terminal electron donor/



**Figure 3. MFC reactor designs for catholyte electrosynthesis**

cuboid geometry with an external catholyte collector (A), cuboid geometry with a partially submerged cathode (B), cylindrical geometry with an internal cathode (C), and cylindrical geometry with an external cathode (D).

acceptor. Externally applied potential (and/or current) provided by the electrochemical apparatus, such as a potentiostat, gives control over the chronoamperometric measurement to poise the working electrode potential and observe the resultant transformation(s). In MFCs, such potential bias—perhaps with a lower signal fidelity—can be introduced by another MFC via an additional set of smaller electrodes inside both the anodic and cathodic half-cells, named third and fourth pins, respectively; this allows biasing from external sources (Figure 2) allowing additional control and modulation functionalities. Described by Ieropoulos et al., third pin is an additional electrode inserted into the anode half-cell to indicate that it is the third electrode added inside the MFC. Third pin is the bias point for modulation from an external source, which could be an additional MFC (named driver cell). The fourth pin is the additional electrode in the cathode, that is enabling modulation of the cathode half-cell through the connection to the external MFC driver cell ((Ieropoulos et al., 2018), Patent no. WO2016120641A1). The novel approach into half-cell potential modulation will be discussed in this perspective as part of the multi-functionality of the MFC as a self-sustainable biorefinery platform where the sole driving force is the microbial metabolism.

### WORKING PRINCIPLES

In the MFC operation, each electron transferred to the cathode electrode via the external circuit, recombines with a corresponding cation transported through the membrane or electrolyte in membrane-less systems and the oxidizing agent present in the cathodic half-cell. However, due to the high concentration of cations in the subject wastewater, it is primarily cation species other than protons that are responsible for the transport of positive charge, leading to the accumulation of cations and increased conductivity in the catholyte (Rozendal et al., 2006). Both cations and protons, being charged species, attract molecules of water that move with them toward the cathode; this occurs due to the electroosmotic drag, a topic thoroughly studied in the field of chemical fuel cells (Zawodzinski et al., 1995). Electroosmotic drag depends on separator properties as well as drag coefficients that is different for hydrogen ions and other cations (Pivovar, 2006). Recently in the field of MFCs, the electroosmotic drag was observed as a particularly interesting phenomenon to study, which is focusing on water recovery from various types of wastewater and the electro-synthesis of liquid catholyte in a previously empty chamber (Gajda et al., 2014, 2015). Formation of liquid catholyte through the osmotic and electro-osmotic forces also provides self-hydration of the open-to-air cathode and maintains the membrane in a hydrated state, something that had already been observed in a long-term study of 12 years, (unpublished data) and more recently substantiated in Gajda et al., 2018. This is particularly important in large-scale applications and long-term operation, where water molecules coming from the anode prevent membrane drying, which can lead to a decrease in ionic conductivity. Self-hydration of the cathode and consequent continuous production of the catholyte prevent precipitation and subsequent cathode fouling occurring at the cathode surface, keeping long-term (>1 year) functionality (Gajda et al., 2020b).

In addition to the ion transport and electroosmotic drag made possible through microbial electroactivity at the anodic half-cell, an important contributor in self-driven electrosynthesis is the cathodic ORR. ORR in the cathode results in the formation of hydroxide ions ( $\text{OH}^-$ ) through the peroxide pathway (Kinoshita, 1988).  $\text{H}_2\text{O}_2$  electrosynthesis is immediately followed by concomitant hydrogenation or decomposition to water, which limits  $\text{H}_2\text{O}_2$  development (Edwards et al., 2009) resulting in cathodic pH increase. At the same time, the anodic pH decreases due to the microbial degradation and electrochemical oxidation of organic fuels, thus resulting in pH splitting and transformation of substrate. The importance of ion transport accompanied by electroosmotic drag and formation of hydroxide at the cathode brings several important aspects to attention, such as the possibility of water recovery through desalination of urine (Gajda et al., 2020c), recovery of nutrient rich solutions (Kuntke et al., 2014), and production of disinfectant (Gajda et al., 2016). Depending on the substrate, MFC configuration and type of the separator used, bioreactor multi-functionality is achieved, whilst producing electrical power. The MFC technology can therefore be used as a platform technology in several other applications that include electrosynthesis of caustic compounds for  $\text{CO}_2$  scrubbing, water purification and disinfection, power generation, and energy storage. For example, the electrosynthesis of salts such as sodium bicarbonates (trona) or potassium bicarbonates (kalicinite) has already shown recovery of elements such as Na and K from the anolyte and the transformation into newly synthesized products on the cathode, whilst generating—not consuming—electricity by the MFC. A similar approach would include the production of target disinfectants, nutrients, fertilizers, recovery of water as shown in previous MFC studies but also targeting new transformation pathways due to the introduction of the half-cell redox potential modulation, via the pins that can also be self-driven.

## BIOREACTOR DESIGN FOR ELECTROSYNTHESIS OF CATHOLYTE

Various MFC reactor design have been investigated and are detailed in the literature (Choudhury et al., 2017; Flimban et al., 2019). However, the majority of the MFC design work has been focusing on the enhancement of power output and/or treatment efficiency. For the electrosynthesis of newly formed catholyte, a different approach should be adapted for improving both quantity and quality of catholyte.

For example, single chamber MFC units with an open-to-air cathode are a popular design choice for system scale-up and ease of maintenance. However, multiple studies have reported the accumulation of precipitates such as carbonates formed by combined ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  with carbonate anions on the cathode surface, which is a strong evidence of the cation migration. Poor proton transfer would result in the formation of caustic agents such as NaOH and KOH that subsequently react with carbon dioxide. As a result, carbonates and bicarbonates are formed on the air side of the cathodes (Ma et al., 2014; Santini et al., 2015). Accumulation of carbonate compound precipitates can lead to cathode fouling and deactivation even only after 60 days in an open-to-air cathode (Santini et al., 2017) although it has been reported that this can be combated *in situ* (Pasternak et al., 2016).

Therefore, when designing MFC reactors for catholyte production, adequate sealing of the cathode chamber to regulate the evaporation rate and oxygen availability should be considered. Unsheltered open-to-air cathode chambers are prone to evaporative losses of catholyte. If the evaporation rate of catholyte is faster than the catholyte production rate, salt deposition on the cathode and separator occurs, which could lead to fouling and decreased performance (An et al., 2017). Appropriate designs of air cathode chambers that enable the formation of liquid catholyte and maintenance of the cathode-membrane interface as a hydrated state would also lead to active extraction of catholyte as a filtrate.

Figure 3 shows examples of MFC reactor configurations that encourage electrosynthesis of liquid catholyte in initially empty chambers. The common two-chamber cuboid type can be used after attaching a catholyte collector (Figure 3A). This design allows the separation of catholyte from the air cathode thus utilizing the whole cathode surface for atmospheric oxygen reduction. Instead of the separate catholyte collection part, electrosynthesized catholyte can be collected from inside the cathode chamber (Figure 3B), thus maintaining a liquid bridge across the separator and the cathode. Also, the already synthesized catholyte that has high concentration of cations, can contribute to the electroosmotic drag. The cylindrical type, either with the cathode on the inside (Figure 3C) or outside (Figure 3D) can benefit from larger cathode surface area and larger separator contact area. These designs are also easily scaled up through stacking multiple reactors in all three dimensions. Such a modular approach would support the purpose of practical implementation in real world scenarios. The catholyte, as newly formed filtrate in the initially empty chamber, demonstrates the self-driven recovery and transformation of chemical species within the aqueous electrolyte as long as electricity is being produced within the MFC.

## CONTROLLING ELECTROSYNTHESIS USING ADDITIONAL ELECTRODES

Electrosynthesis in MFCs is directly influenced by the rate of electron transfer, which correlates with the rate of cation migration, electroosmotic drag as well as the rate of ORR. The separator also plays an important role in electrosynthesis, since the type (ion selective or not), composition, thickness and porosity have a major influence on both the quantity and quality of synthesized catholyte (Merino Jimenez et al., 2017; Merino Jimenez et al., 2019), as well as the current production rate. Other factors such as electrode material and catalysts for both electrodes and separators can significantly influence the process as well. Feedstock composition is another key factor since the concentration of elements such as nitrogen, phosphorus, potassium, sodium, and calcium (N, P, K, Na, Ca), determines recovery rates of the target cations on the cathode. Therefore ion-rich waste streams such as urine would be ideal sources for both energy and nutrient extraction. In this section, a novel approach to control the MFC electrosynthesis is discussed.

Since the electrode potential together with current are important factors for electrosynthesis (Table 1), they should be carefully monitored and controlled during the reaction. For example, it was reported that applying a range of potentials on metallic copper surfaces resulted in a total of 16 different products from  $\text{CO}_2$  reduction (Kuhl et al., 2012). This is achievable using electrochemical equipment such as potentiostats, but this would require external energy to run. Alternatively, here we suggest a new method using additional electrodes in MFCs (Patent no. WO2016120641A1), so called third and fourth pins for the anode and cathode chambers respectively (Figure 2), for modulating the physiochemical conditions of MFCs

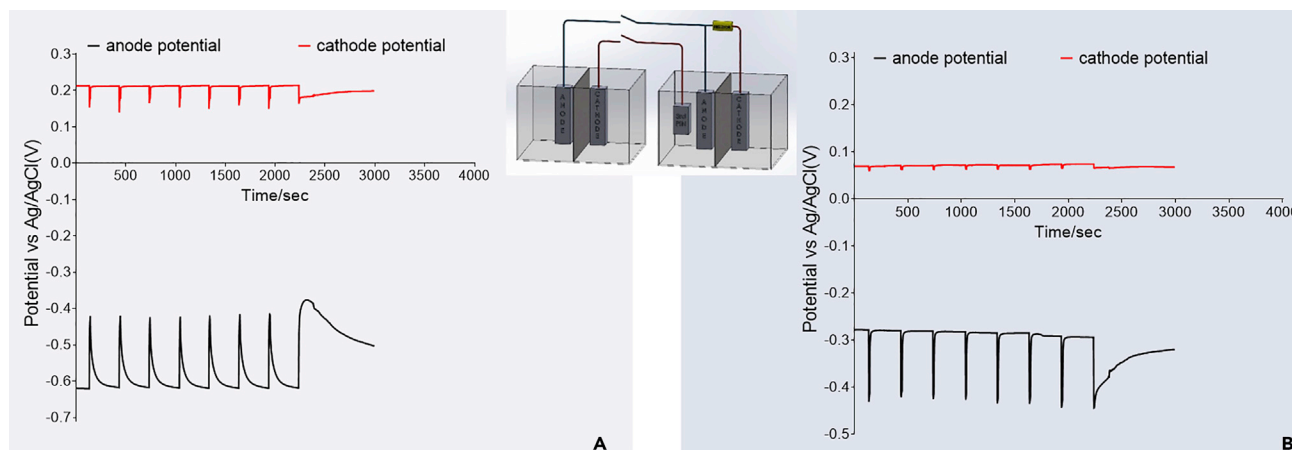
**Table 1. Standard potentials for selected reduction half-reactions in aqueous solutions at 25°C.**

Half-reaction	E <sup>0</sup> (V vs. NHE)	Half-reaction	E <sup>0</sup> (V vs. NHE)
F <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ 2HF	3.053	2H <sup>+</sup> + 2e <sup>-</sup> ⇌ H <sub>2</sub>	0.000
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ 2H <sub>2</sub> O	1.763	Fe <sup>3+</sup> + 3e <sup>-</sup> ⇌ Fe	-0.040
NiO <sub>2</sub> + 2e <sup>-</sup> ⇌ Ni <sup>2+</sup> + 2H <sub>2</sub> O <sup>-</sup>	1.590	O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> ⇌ HO <sub>2</sub> <sup>-</sup> + OH	-0.080
MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> ⇌ Mn <sup>2+</sup> + 4H <sub>2</sub> O	1.510	Pb <sup>2+</sup> + 2e <sup>-</sup> ⇌ Pb	-0.125
Mn <sup>3+</sup> + e <sup>-</sup> ⇌ Mn <sup>2+</sup>	1.500	O <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup> ⇌ HO <sub>2</sub>	-0.130
MnO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ Mn <sup>2+</sup> + 2H <sub>2</sub> O	1.230	CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ HCOOH	-0.200
O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> ⇌ 2H <sub>2</sub> O	1.229	Ni <sup>2+</sup> + 2e <sup>-</sup> ⇌ Ni	-0.257
Cu <sup>2+</sup> + 2CN <sup>-</sup> + e <sup>-</sup> ⇌ Cu(CN) <sub>2</sub> <sup>-</sup>	1.120	PbSO <sub>4</sub> + 2e <sup>-</sup> ⇌ Pb + SO <sub>4</sub> <sup>2-</sup>	-0.351
Br <sub>2</sub> + 2e <sup>-</sup> ⇌ 2Br <sup>-</sup>	1.087	Cr <sup>3+</sup> + e <sup>-</sup> ⇌ Cr <sup>2+</sup>	-0.424
NO <sub>3</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> ⇌ NO + 2H <sub>2</sub> O	0.960	Fe <sup>2+</sup> + 2e <sup>-</sup> ⇌ Fe	-0.440
Pd <sup>2+</sup> + 2e <sup>-</sup> ⇌ Pd	0.915	S + 2e <sup>-</sup> ⇌ S <sup>2-</sup>	-0.447
2Hg <sup>2+</sup> + 2e <sup>-</sup> ⇌ Hg <sub>2</sub> <sup>2+</sup>	0.911	Cr <sup>3+</sup> + 3e <sup>-</sup> ⇌ Cr	-0.740
NO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + e <sup>-</sup> ⇌ NO <sub>2</sub> + H <sub>2</sub> O	0.800	Zn <sup>2+</sup> + 2e <sup>-</sup> ⇌ Zn	-0.763
Fe <sup>3+</sup> + e <sup>-</sup> ⇌ Fe <sup>2+</sup>	0.771	2H <sub>2</sub> O + 2e <sup>-</sup> ⇌ H <sub>2</sub> + 2OH <sup>-</sup>	-0.828
O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ H <sub>2</sub> O <sub>2</sub>	0.695	Cr <sup>2+</sup> + 2e <sup>-</sup> ⇌ Cr	-0.900
MnO <sub>4</sub> <sup>-</sup> + e <sup>-</sup> ⇌ MnO <sub>4</sub> <sup>2-</sup>	0.560	2SO <sub>4</sub> <sup>2-</sup> + H <sub>2</sub> O + 2e <sup>-</sup> ⇌ SO <sub>3</sub> <sup>2-</sup> + 2OH <sup>-</sup>	-0.940
Cu <sup>+</sup> + e <sup>-</sup> ⇌ Cu	0.520	Fe(CN) <sub>6</sub> <sup>4-</sup> + e <sup>-</sup> ⇌ Fe + 6CN <sup>-</sup>	-1.160
O <sub>2</sub> + 2H <sub>2</sub> O + 4e <sup>-</sup> ⇌ 4OH <sup>-</sup>	0.401	Mn <sup>2+</sup> + 2e <sup>-</sup> ⇌ Mn	-1.180
Fe(CN) <sub>6</sub> <sup>3-</sup> + e <sup>-</sup> ⇌ Fe(CN) <sub>6</sub> <sup>4-</sup>	0.361	Al <sup>3+</sup> + 3e <sup>-</sup> ⇌ Al	-1.676
Cu <sup>2+</sup> + 2e <sup>-</sup> ⇌ Cu	0.340	Mg <sup>2+</sup> + 2e <sup>-</sup> ⇌ Mg	-2.356
Cu <sup>2+</sup> + e <sup>-</sup> ⇌ Cu <sup>+</sup>	0.159	Ca <sup>2+</sup> + 2e <sup>-</sup> ⇌ Ca	-2.840
S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> + 2e <sup>-</sup> ⇌ 2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.080	K <sup>+</sup> + e <sup>-</sup> ⇌ K	-2.925
NO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O + 2e <sup>-</sup> ⇌ NO <sub>2</sub> <sup>-</sup> + 2OH <sup>-</sup>	0.010	Li <sup>+</sup> + e <sup>-</sup> ⇌ Li	-3.045

Data from (Arning and Minteer, 2007).

including redox potential. Potential use of this method for power boosting and open circuit potential (OCP) sensing has previously been reported (Ieropoulos et al., 2018). The idea is that the additional “pin” electrodes are used as the bias points, on which the application of a specific potential can modulate the half-cell redox potential of the anolyte or catholyte. In addition, measured potential difference between the third and fourth pin electrodes can reflect the true real redox potential difference between the anolyte and catholyte since the pin electrodes are not in direct contact with the working anode and cathode electrodes and therefore decoupled from the main load-bearing circuit. The biasing via a pin depends heavily on the pin size (relative to the main electrodes) and the impedance imposed by the electrolyte, which in turn allows the redox level to be estimated. The principle of the additional electrode being inserted into the anode half-cell (third pin) and the additional electrode in the cathode half-cell (fourth pin) is to enable a connection between a separate MFC (driver) to the main MFC (working cell) via the pin electrodes.

Figure 4A shows the half-cell potential of the driver cell (measured vs Ag/AgCl, 3 M KCl) during the connection and disconnection with another MFC via an additional pin electrode in the anode (third pin). The moment of connection resulted in anodic potential shift into more negative values, from -0.277 V down to -0.443 V (Figure 4B) while the anodic potential of the driver cell (Figure 4A) shifted into a more positive potential from -0.620 V to -0.422 V. The cathode of the working cell shows no significant change by the applied bias as the target half-cell was the anode. The MFCs used for this test were assembled using 50 mm tall ceramic cylinders, carbon veil anodes and activated carbon cathodes as previously described (Gajda et al., 2020a), inoculated with activated sewage sludge/urine mixture and operated with 100% human urine. The pin electrode was made of the same carbon veil material as the main anode electrode with the size being 20× smaller in order to fit into the chamber; normally pin electrodes are 1/10 of the size of the main electrode, but here they were smaller due to the available space. Pin electrodes were fabricated by folding the electrode material, piercing stainless steel wire for the connection point and wrapping



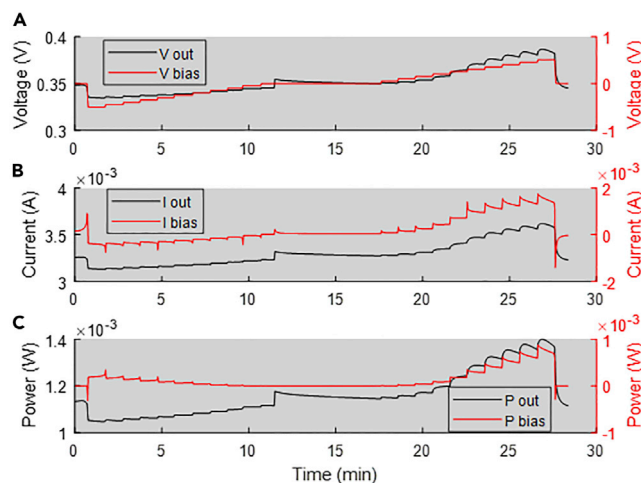
**Figure 4. Controlling electrosynthesis using additional electrodes**

Half-cell potentials of a driver MFC (A) and a working cell (B) poised through the third pin in the anodic chamber. Poising performed by connecting and disconnecting the working and driver cells 7 times at fixed time intervals (connection cycle: 10 s on, 300 s off), whilst the eighth lasted longer.

the pin in parafilm to form a sleeve in order to prevent direct contact with the main electrode. The pin was placed in the anodic electrolyte and connected to the logging equipment.

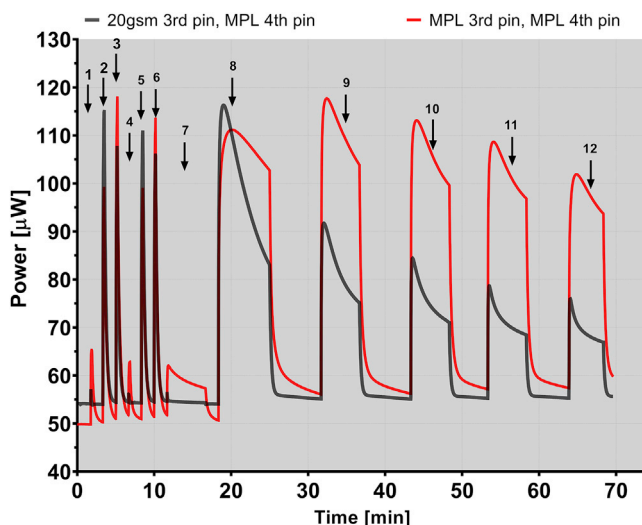
The driver cell could either be in an active current loop, or in open circuit. In the above demonstration, the driver cells were used explicitly for the function of periodically driving the working cells. The advantage of this configuration is the utilization of cell recovery (after being polarized) and of the capacitive properties of MFCs (Ieropoulos et al., 2005; Walter et al., 2020), which allows a repeated instantaneous delivery of proportionately high-energy bursts. This is visible in Figure 3A, in which the driver waveform resembles a discharging capacitor.

Tests have also been carried out using a precision power supply, as opposed to a second “driver” MFC, in order to verify that similar characteristics of potential and power increase can be achieved when poised via an additional third pin in the anode (Figure 5). Here, the power of the working cell increased from 1.16 mW



**Figure 5. Poising via an additional third pin in the anode**

Input bias to, and output potential (A), current (B) and power (C) from a working MFC, poised through the third pin in the anode chamber. Poising performed by a precision power supply from  $-0.5$  V to  $+0.5$  V, incrementing in 60s intervals, and held for 10 min at 0 V bias.



**Figure 6. MFC power output when under third and fourth pin bias**

20gsm carbon veil third pin and MPL fourth pin (black line), MPL used as both third and fourth pin (red line). Numbers indicate pin connection and different time intervals; 1 & 4 - third pin ON only; 2 & 5 - fourth pin ON only; 3 & 6 - both third and fourth pin ON; 7 - third pin ON only; 8 & 12—fourth pin ON only; 9, 10 & 11—both third and fourth pin ON. Connection cycle for 1–6: 10 s ON, 300 s OFF. Connection cycle for 7: 10 min ON, 5 min OFF, Connection cycle for 8–12: 10 min ON, 10 min OFF.

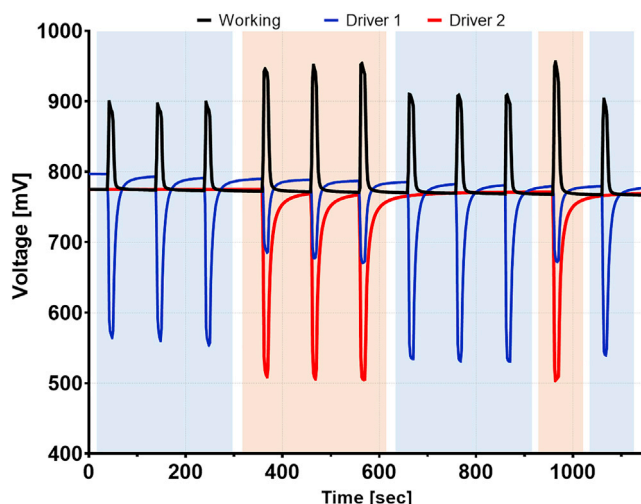
to 1.4 mW which is ca. a 21% increase, whereas the current went up from 3.32 mA to 3.62 mA, which is a 9% increase. The low anodic potential developed by a non-poised MFC is similar to the standard redox potential for oxidation (by microorganisms) of carbon-based substrates, such as  $-0.28$  V for acetate and  $-0.43$  V for glucose (Madigan et al., 2000). Where the anodic potential can be adjusted, work by Torres et al. demonstrated that electrodes at the lowest potentials showed a faster biofilm growth and produced the highest current densities, whilst the positive potential favored the development of a non-electroactive biofilm (Torres et al., 2009). Good power production is governed by anaerobic respirators that are able to use terminal electron acceptors with a low redox potential (Grüning et al., 2015).

It can therefore be deduced that potentially, the required electric charge for specific electrochemical reactions (Table 1) can be supplied by either another MFC or a precision apparatus but importantly via the additional pins. While the electron-uptake by bacterial cells is the key step in MES of  $H_2$  and  $CH_4$ , varying the cathode redox potential levels can lead to different reactions, consequently resulting in different rates of electron transfer. In order to achieve a higher  $CH_4$  production rate, cathode potential levels below  $-0.6$  V (vs. SHE) are usually employed (Li et al., 2020).

### PROPOSED MODULATION OF PIN ELECTRODE PERFORMANCE

The use of microporous layer (MPL) to functionalize carbon fiber veil, has been shown to positively affect power production when used on the anode (You et al., 2014) or cathode (Gajda et al., 2014; Papaharalabos et al., 2013; Santoro et al., 2011). MPL as pin material promotes charge transfer from the driver to the working cell. This can be seen in Figure 6 where two working cells were constructed, one using carbon veil third pin and MPL fourth pin, while the second working cell had MPL pins in both half-cells. The anode electrodes of both working cells were made of carbon veil (carbon loading:  $20\text{ g m}^{-2}$ ). The duty cycle of the drivers connecting only third pins, only fourth pins, or both at the same time indicates how the working MFC can be controlled in both chambers and how the pin material is affecting the bias. The results indicate that the large-specific surface area materials are key components for the effective application of MFC-originated potential bias. Relative size or dissimilarity of pin material to either anode or cathode electrodes might also have an effect on its performance. As expected, a more positive material in the anodic chamber (in comparison to negative anode material) creates a higher overall negative potential in the anode, once in a current loop. Similarly, a more negative material in the cathode results in overall higher positive potential.





**Figure 7. MFC voltage when poised via two additional electrodes (third pins) in the same anodic chamber**

Blue colored regions—one driver MFC (Driver 1) connected; orange colored regions—two driver MFCs (Driver 1 and Driver 2) connected to the working cell. Connection cycle: 10 s on, 100 s off.

A plurality of driver and/or working cells may be a good way of modulating MFC potential for electrosynthesis. Figure 7 shows that working cell voltage increased by  $23.5 \pm 0.8\%$  when poised by two drivers in comparison to  $17.2 \pm 1.1\%$  increase when poised by a single driver. The superposition of plurality of drivers or working cells does not result in linear increments of power due to the nonlinearity of the energy transfer processes involved. A similar phenomenon may be possible when multiple working cells are connected with a single driver that is relatively strong (more negative or positive potential). Behaviors and effects of the pins in MFC stacks, whose main electrodes are connected in series and/or parallel, should be studied further as should multifunctional MFC unit network configurations via multiplexing. Furthermore, external load(s) of both working and driver cell and connection duty cycles are also deemed important in effecting modulation.

This is a novel method and still much of it is unknown, as the redox potential measurement in natural and organic-rich water bodies is affected by multiple metabolic and environmental factors making the redox conditions difficult to investigate (Sigg, 2000). In a way, it is akin to electro-fermentation but happening in a setting where bias can result in resource recovery and energy production. Therefore, in-depth investigation of this novel technique is needed and indeed forms part of the immediate future objectives of this line of work.

### CHALLENGES AND VIABILITY

With increased knowledge of the reaction chemistry, it is possible to imagine designing electrochemical cells capable of recovering/producing desired products selectively and efficiently. The technology to electrochemically convert waste to fuel and other value-added products would be a significant step towards a more sustainable future; hence, the recent focus on electro-synthesis and electro-fermentation by the wider scientific community. Given this research field is relatively new, further investigation to understand its potential and working mechanisms is needed. Efforts should be made to achieve high selectivity of target compounds, fast reaction rates, as well as simple and economical separation of the desirable product from the solution. Although electro-synthesis in the laboratory is a prerequisite for the development of a commercial process, this is not always transferable to a manufacturing scale-up process and commercial uptake. Therefore, scale-up work should be carried out with commercialization in mind. Long-term performance, materials, capital and running costs, and environmental impact are critical for successful exploitation. For example, MES focused around bioproduction of short and medium chain fatty acids from  $\text{CO}_2$  is electricity-driven, which results in high operating costs and low product specificity (PrévotEAU et al., 2020) and in turn hinders its application.

Therefore, the energy cost for MES operation may pose another challenge for scaling-up. The positive energy-balance in appropriately optimized and scaled-up electricity-producing MFC systems would be the platform where the presented strategies for modulation through additional electrodes could be self-sustainable or self-driven. This would be an important advantage in terms of operating costs and energy produced, not consumed. Moreover, the formation of liquid catholyte prevents precipitation and fouling, maintains optimal ion transport and enables the chemical and biological synthesis processes to happen. Currently, the caustic environment on the cathode offers limited opportunities in unbiased conditions; however, the control of the electrode potential may facilitate the production of a variety of different products. It is unknown how changing the half-cell potential would affect the catholyte generation as well as the physico-chemical properties of the filtrate therefore this should be further studied. MFCs can be successfully scaled-up for practical applications (Ieropoulos et al., 2010, 2013; Tender et al., 2008), for the purpose of treatment (Babanova et al., 2020) and off-grid power (Ieropoulos et al., 2016). The practical aspect of scaling up MFC technology goes beyond the production of off-grid energy from waste in also improving sanitation, safety and public acceptance (You et al., 2020). It is envisaged that the development of MFC-centered multifunctional platforms will aid circular economy, where aspects of electrosynthesis could be tailored for the desired target process in a given environment.

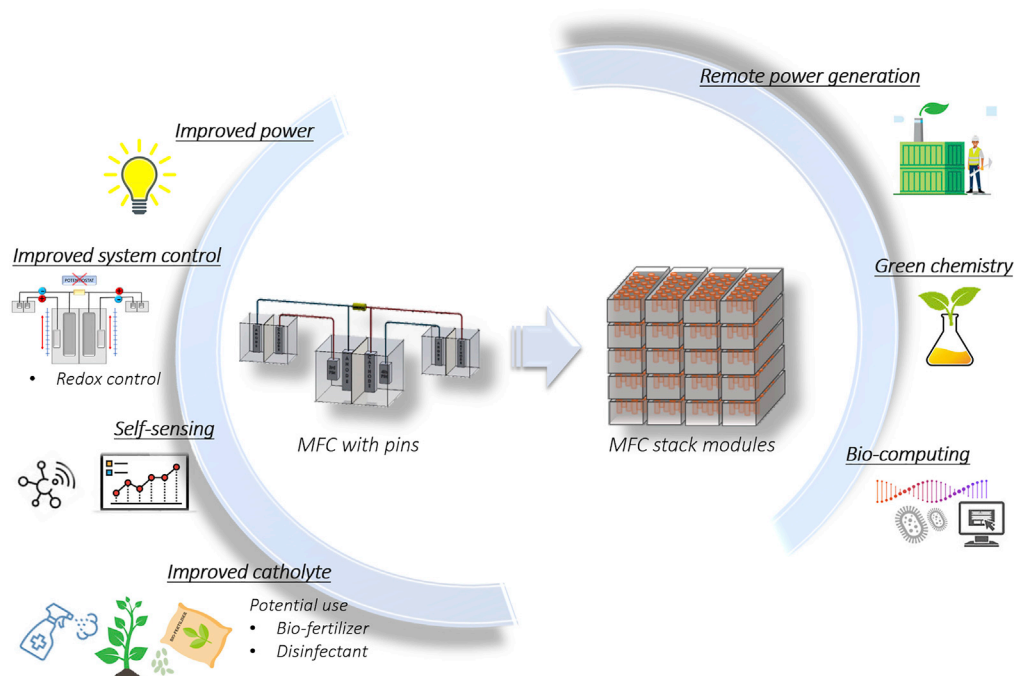
The introduction of additional electrodes (*pins*) inside the two MFC half-cells allows for unique connectivity with external devices, bringing a bias directly inside the anolyte and/or catholyte, which can result in the selective recovery of metals and nutrients, depending on the half-reaction potential. More importantly perhaps, this can allow output modulation (i.e. amplification or attenuation), thereby controlling the quality of the MFC output signal, which could (for example) be used in conjunction with pulse-width-modulation circuitry. In the case of MFC stacks and as part of a multi-functional approach, unit operation can toggle between “working” and “driver” MFC modes—a process that can be facilitated by multiplexing. The ability to measure, in real-time, the true difference between an anolyte and a catholyte’s redox potential values, whilst generating current is a significant advantage in terms of system monitoring and optimization and one that does not require the circuit to be broken in order to measure OCV (self-sensing). Self-sensing and controlling the occurrence of potential difference as a result of crossover processes and H<sup>+</sup>/OH<sup>-</sup> migration should also be considered as an additional measure of system efficiency for target applications. Scaling up of this system will be needed for meaningful yield bringing about opportunities of wider range of control. If achieved, self-controlled and self-driven electroseparation would be possible. Simply inserting these additional electrodes into an otherwise standard MFC can enable real-time oscillation, which can be beneficial for the purposes of maximum power transfer (Ieropoulos et al., 2008; Papaharalabos et al., 2013). Taking into account all of the aforementioned possibilities, the approach described here could render the BES/MFC a true platform technology for the future, as conceptualized in Figure 8.

In summary, the following points are still needed to be addressed to take this approach forward:

- Understand the working mechanisms and characteristics such as relations between physico-chemical properties of the filtrate and modulated potentials
- Increase selectivity of target compounds and reaction rates
- System scale-up and long-term field test whilst maintaining lab test performance
- Reduce material cost, running costs and environmental impact

## CONCLUSIONS

In this perspective, we present an innovative concept of electrosynthesis that can coexist within the electricity-producing MFC bioreactors thanks to electrochemical processes such as electroseparation of cationic species, electroosmotic drag, and ORR. This can provide a platform for microbially assisted electrosynthesis of target compounds within the cathode half-cell. Moreover, *in situ* signal modulation and control can be achieved using a novel design engineering method, through the introduction of additional “pin” electrodes. Through this modulation method we can adjust the electrode potential of each of the half-cells through the pin electrodes transferring incoming charge from another MFC source. In this way, the potential modulation could become self-sustainable.



**Figure 8. Prospects of electroseparation in microbial fuel cells being capable of *in situ* modulation using additional “pin” electrodes**

### LIMITATIONS OF THE STUDY

The concept of MES using MFCs is a new research field that has only recently been reported. In this work, we present our perspective on this approach for waste-to-resource and introduced the use of additional pin electrodes as a method of fine *in situ* modulation of MFC operation, including electrosynthesis. Although the new MFC design with additional pin electrodes for modulation and control, is supported by initial experimental results, some of which are also presented here, further investigation is required to characterize the material for pin electrodes relative to that of working anodes and cathodes. In particular, further exhaustive experiments are required to define parameters such as distance from the working electrodes, type of insulation between the pin and working electrodes, periodicity of modulation, as well as: type of connectivity; value of external load; feedstock type and supply rate and of course, different types of anodic communities, during modulation. This study was also limited in terms of optimization of specific redox levels for specific target compounds. In addition, although this is still early-stage experimentation, it would be invaluable to perform life cycle and economic assessments of this particular configuration of the technology, also in comparison to other electrosynthesis technologies, which will provide better insights into future research directions.

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### AUTHOR CONTRIBUTIONS

Conceptualization of pin electrosynthesis, I.A.I. and J.G.; subsequent electro-filtration conceptualization, I.G.; investigation, I.G., J.Y., and A.M.; writing-original draft, I.G., J.Y., and A.M.; writing-review & editing, J.G. and I.A.I.

### DECLARATION OF INTERESTS

I.A.I. and J.G. have a patent (no. WO2016120641A1) related to part of this work, which is mentioned in the main text. The other authors declare no competing interests.

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