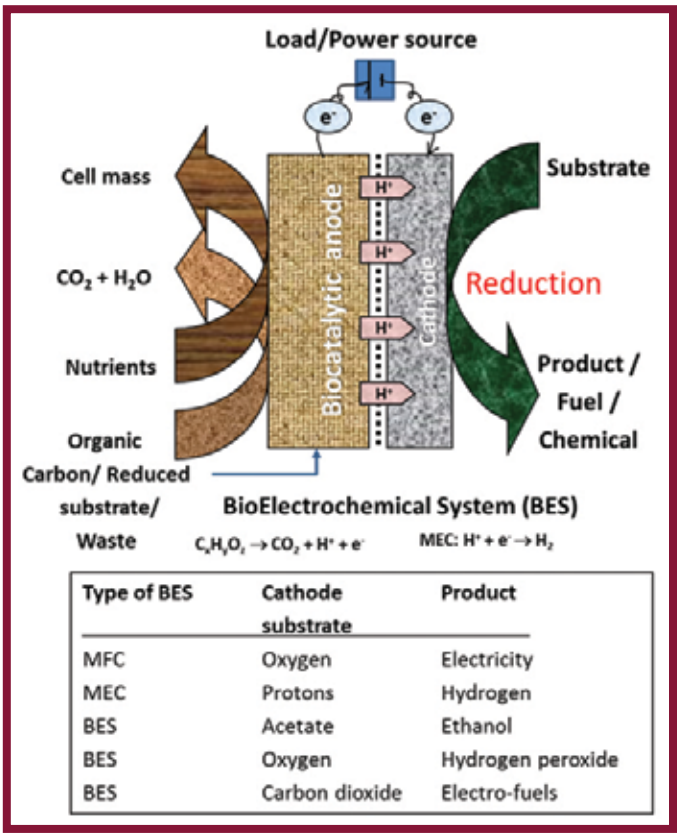
# Microbial Fuel Cells and Microbial Electrolyzers

*by Abhijeet P. Borole*

Microbial fuel cells are electrochemical devices that use microbes as catalysts instead of inorganic catalysts to drive the anodic and/or cathodic reactions to produce electricity.[1] The field of microbial fuel cells (MFCs) was initially focused on wastewater treatment, but has evolved into a much more diverse field of research called Bioelectrochemical Systems (BES). Microbial electrolyzers or microbial electrolysis cells (MECs) are a different manifestation of BES that generate hydrogen using less than half the voltage or electrical energy needed for conventional water electrolysis. The reduced electrical input is enabled by the chemical energy that comes from organic or reduced inorganic substrates that serve as the feedstock for hydrogen production in MECs. Electrons are extracted from the substrates and converted into hydrogen at the cathode, operating at room temperature. The cathode catalysts can be metal-based or biological in nature. Figure 1 shows a generalized configuration of the BES. The versatility of the BES platform shown in the figure illustrates the potential of this approach to produce not only electricity and hydrogen but also biofuels, chemicals and bioproducts.

## Electrocatalysis-Biocatalysis Synergy

Fuel cells have set a high mark for energy efficiency among the various renewable energy production options that have evolved over the last few years. The high efficiency comes from the molecular nature of electrocatalysis. In comparison to thermocatalysis, where vibrational energy is used to increase the rate of reaction, electrocatalysis has a significant advantage, because voltage is the driving force for reactions in addition to temperature, which minimizes the energy losses to the environment, thereby improving the conversion efficiency. Biocatalysis is another low temperature catalytic process that works at the molecular level by overcoming the energy of activation via structural re-combination of reactants that self-assemble into catalytic sites. Combining electrocatalysis with biocatalysis in the bioelectrochemical approach employed in BES results in a significant synergy, improving efficiency significantly. This is because of the continuity of the electron flow from the substrate to the product, afforded first, via the biocatalytic reaction, and then by the electrocatalytic reaction, resulting in a continuous path within the electrical circuit. This mechanism is supported by the relatively recent discovery of electrical communication between biological systems and electrodes. Biological nanowires have been identified to enable efficient electron conductance between inorganic substrates and organic or biological entities. Pili-based nanowires have been identified in *Geobacter sulfurreducens* and *Shewanella oneidensis*, which are capable of electron transfer from microbes to an anode.[2,3] Direct interfacing of electron producers and electron sinks has given rise to this high degree of efficiency evidenced in microbial fuel cells. Similarly, MECs also have high efficiency, shown by the generation of hydrogen from acetate using microbes at a Coulombic efficiency above 90% and an overall energy efficiency as high as 82%.[4]




| Type of BES | Cathode substrate | Product |
|---|---|---|
| MFC | Oxygen | Electricity |
| MEC | Protons | Hydrogen |
| BES | Acetate | Ethanol |
| BES | Oxygen | Hydrogen peroxide |
| BES | Carbon dioxide | Electro-fuels |

**Fig. 1.** *Schematic of bioelectrochemical systems including MFCs and MECs.*

## Relevance to Energy Production in the 21st Century

The field of BES has given rise to an increasing number of opportunities for collaborations between electrochemists, biologists, and engineers. This has brought together a unique opportunity for these three communities to work together and contribute to the advancement of the field. MFCs originated as a potential solution to wastewater treatment a decade ago. Water has become an increasingly scarce commodity during the last decade. Zero-energy wastewater treatment is one vision for the scientists working in the area of BES development. This is one of the many components of the water-energy nexus issues that the USA is currently facing. Synergy of BES with biorefineries has also been identified, with potential improvement in the efficiency of conversion of biomass to energy.[5] Hydrogen production has been pursued from various renewable sources including solar, wind power, and biomass, etc. Economically competitive production of renewable hydrogen, however, has been a challenge. MECs offer a new, energy-efficient method for hydrogen production from biomass and waste. The ability to produce hydrogen from waste and biomass hydrolysis products, namely sugars and organic acids has been demonstrated.[6] Conversion of lignin-degradation products, phenolic compounds, and furan aldehydes at the bioanode has also been demonstrated.[7] This opens the door to the possible conversion of essentially all components of biomass to hydrogen using MECs.

## Economic Considerations

Economic feasibility of BES can come from one of three ways. While the primary function of these systems is energy production, worthwhile benefits can be realized from their contribution to reduction in waste and/or production of clean water (Fig. 2). A current

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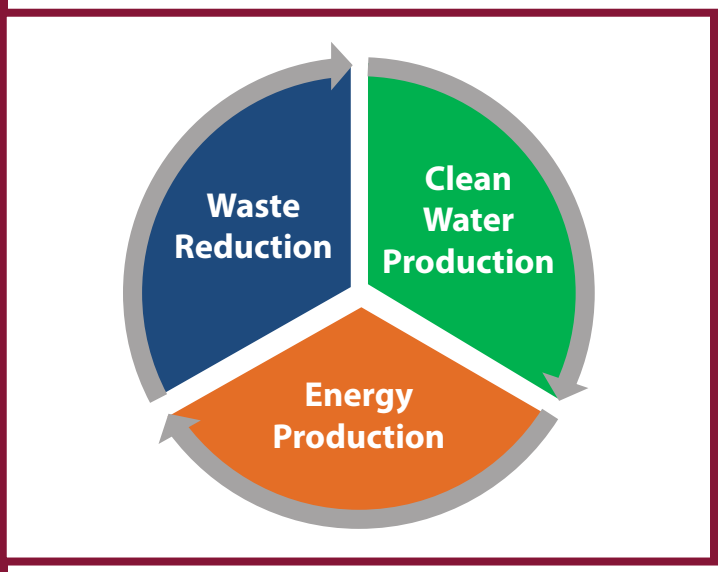


**Fig. 2.** *Three potential benefits of BES technology contributing to economic feasibility.*

density of 25 A/m$^2$ has been suggested as a threshold for economic feasibility of MFCs,[8] possible with reduction in internal electrical resistance below 40 mΩ m$^2$. Electricity as a product from MFCs may not by itself justify the costs of implementing these systems, however, removal of key contaminants or production/recycle of water at zero energy cost would warrant use of these systems.

Microbial electrolyzers, on the other hand, generate renewable hydrogen that is valued higher than electricity and thus have a greater potential to reach economic feasibility. A comparison of MEC technology against other existing technologies for hydrogen production is shown in Table I.

Among the renewable energy technologies included in Table 1, MECs are observed to be a relatively cost competitive alternative, however this technology is nascent and significantly more effort is required to reduce the costs down to the \$2/kg $H_2$ set by the U.S. Department of Energy (DOE) (not including hydrogen storage and delivery costs). Specific cost reduction goals set by the DOE Fuel Cell Technology Office (FCTO) include reduction in cathode costs to \$50/m$^2$ and a target rate of hydrogen production equal to 4 L-$H_2$/L-reactor-day by 2020. The current densities necessary for MECs to be economically feasible have been reported to be on the order of 20 A/m$^2$.[8] A few studies have shown this to be achievable,[13] although not in long-term studies.

## Scaling-up BES

While the results from laboratory scale studies of BES have been encouraging, the demonstration of their potential for practical application has been lagging. A few investigations targeting pilot-scale studies of MFCs and MECs have shown significantly lower performance compared to laboratory-scale systems. This is due to poor understanding of the scale-up parameters. The lack of identification of electrochemical losses during scale-up is one factor contributing to the poor understanding of MECs and concomitant poor performance of these systems at scale. A number of electrochemical methods have been employed to investigate these losses; however, insufficient work has been done to date to identify which scale-up parameters matter the most and how they should be controlled as the scale of operation increases. Further collaborative work between electrochemists, microbiologists, material scientists, and chemical engineers is needed to advance this field towards commercial consideration.

**Table I. Comparison of cost of hydrogen production.**[9,11]
The costs reported in last column are based on 2003 \$, except for MEC.

| \$/kg $H_2$ | EERE[9,10] | | Literature[8,11] |
|---|---|---|---|
| | 2011 Status | 2015 Target | |
| Wind + Electrolysis | 4.10 | 3.00 | 6.64 |
| PV-Electrolysis | | | 6.18[a] |
| Biomass gasification | 2.20 | 2.10 | 4.63 |
| Biomass pyrolysis | | | 3.80 |
| Solar thermal | NA | 14.80 | |
| Photoelectrochemical cell | NA | 17.30 | |
| Photobiological | NA | 9.20 (2020 Target) | |
| Nuclear thermal splitting of water | | | 1.63 |
| Natural gas reforming | 2.00 | 2.10 | 1.03 |
| Coal gasification | | | 0.96 |
| Microbial electrolysis | NA | 12.43[b] | 5.40[c] |
| Reforming of bio-derived liquids[d] | | | |
| 1. Ethanol | 6.60 | 5.90 | |
| 2. Bio-oil aqueous phase[12] | 31.84 | 3.00[e] (2017 Target) | |

[a]*Based on projected future technology.*
[b]*Derived from [10]. A cost of \$5.18 was deduced from the reported hydrogen production cost of \$12.43, which was for production of substrate via fermentation. The reported cost of electrodes for MEC (\$300/m$^2$, 2015 target set in the multi-year program plan developed by the FCTO),[9] however, does not give estimated cost of hydrogen production. It assumes a hydrogen production rate of 1 L-$H_2$/L-reactor-day (2015 Target).*
[c]*Derived from [8]. This is a projected cost using reduced cost of electrode materials in the future.*
[d]*For conversion of bio-derived liquids to hydrogen via steam reforming.*

## Electrochemical Methods to Study BES

Techniques such as cyclic voltammetry and impedance spectroscopy have been employed to characterize the current generation and electrochemical parameters of BES. The application of electrochemical methods to biological systems warrants development of new ways of analysis and interpretation. While the techniques are well understood by electrochemists, the significance of resulting parameters is better understood by researchers with a background in biology. Many such collaborative teams have originated and reported findings from these systems, however much more work is needed to address the scale-up issues.

***Cyclic voltammetry*** ▸ The use of cyclic voltammetry for studying MFCs/MECs has resulted in identification of the midpoint redox potential at which the bioanodes generate current.[14] This varies depending on the nature of the biocatalyst, which can be a single species such as *Geobacter sulfurreducens* or mixed consortium of species. For the former, the midpoint potential at which catalytic current arises has been reported to be about -0.15 V vs. a Standard Hydrogen Electrode (SHE).[15] In both cases, multiple peaks responsible for catalytic current have been commonly observed.[16] Since bioanodes are living systems, these peaks can change with time and are further influenced by process conditions. This leads to complex characteristics requiring a collaborative effort between microbiologists and electrochemists to delineate the electrochemical changes and relate them to the biology or process conditions. Multiple proteins, including cytochromes and other electron transfer agents present in outer-membrane, have been implicated in the electron transfer process. Pili proteins have been

reported to be responsible for efficient extracellular electron transfer to electrodes, leading to high current densities.[17] Two mechanisms have been reported to explain the process, namely electron super-exchange via cytochromes[18,19] and metal-like conductivity via pili nanowires,[20] both of which may be active in different microbial species or under different process conditions. The electroactive properties of proteins and biofilms create a whole new dimension of applications and their robust and diverse nature can potentially enable industrial applications even beyond MFCs and MECs. The sensitivity of the microbial systems to environmental and growth conditions results in challenges for comparison of the results from multiple laboratories, often requiring careful documentation of conditions and reproduction of data at multiple locations to provide meaningful evaluations during the developmental stage.

***Electrochemical impedance spectroscopy (EIS)*** ▸ EIS is another tool which has been increasingly used to characterize BES and in determining the internal resistance of bioelectrochemical cells and the impedances characteristic of the electrodes and their living components. These analyses have revealed that there are major differences between the impedances of conventional fuel cells and bioelectrochemical cells.[21] First, due to the operation of the BES cell at neutral pH, the cathode charge transfer resistance can be several orders of magnitude higher than, say the PEM fuel cell. Secondly, the impedance of a bioanode harboring a microbial catalyst decreases with time as the density of active sites increases resulting from microbial growth. Additionally, the impedance of the bioelectrodes is a function of the potential, therefore, potentiostatic EIS is more appropriate for studying these systems than EIS at open-circuit conditions. The examination of the BES as full cells operating under closed-circuit conditions vs. half cells poised at specific potentials can provide complementary information and such insights can help to improve systems design.[22,23] The electrochemical parameters obtained via EIS, such as charge transfer resistance, diffusion resistance, double layer capacitance, etc., via equivalent circuit modeling (ECM) correspond to terms that can be obtained via biochemical reaction kinetic analysis and mass transfer process modeling (though appropriate model discrimination and parameter estimation is essential with the ECM approach). The exchange current obtained from measurement of bioanode charge transfer resistance can potentially be related to $k_{cat}$ for electron donor utilization at the anode. Similarly, mass transfer of substrate and products within the biofilms is likely to be related to the diffusion resistance obtained via ECM analysis. These synergistic representations between electrochemistry and biology provide the groundwork for the newly emerging field of bioelectrochemical engineering, which can be envisioned as an exciting opportunity for academicians as well as application engineers who aim to contribute to the BES development and consequently to the 21$^{st}$ century bioeconomy.

***Power management and energy harvesting*** ▸ MFCs produce relatively low voltage for direct powering of devices. Use of stacked cells and larger volume systems have been investigated, however, such configurations result in voltage reversal and inefficient energy harvesting. Use of power management systems (PMS) is therefore necessary to harvest energy efficiently. Such systems have been investigated, however, significant power loss still exists.[24] This is because the components used have not been developed for MFC/BES, but imported from solar, wind power, and other systems, which operate at different electrical outputs. Typical components used in power management systems include capacitors, charge pumps, rechargeable batteries, and boost converters. In addition, continuous energy harvesting of the low power has to be coupled to discontinuous power usage or discharge for powering sensors and other devices. This requires separate, autonomous systems for on-off control, which can themselves consume power. Thus, efficiency of these power management systems has to be high to get net power from MFCs.

The voltage output from BES changes with time and different applications require different modes of energy harvesting. For example, MECs that are used to produce hydrogen have to be operated at maximum current to maximize the hydrogen production rate, while MFCs that are primarily used to produce power have to be operated at intermediate current densities at which maximum power is realized. This requires identification of the maximum power point to harvest energy from MFCs. The energy harvesting regimes and operating voltages can influence the microbial communities and selection of extracellular electron transfer proteins and/or alter the dominant microbes in the communities. Thus, for similar feed conditions, the composition of the bioanode communities can be quite different, for example, in MFCs, where maximum power is tracked, compared to MECs, where maximum current may be of interest. Various combinations of energy storage components have been investigated, however, the efficiency of harvesting is still limited. Three main types of circuits that have been employed include capacitor-based systems, charge-pump based systems and boost converter-based systems. Optimization of energy production from BES requires significantly more work for developing integrated circuits combining multiple electronic components depending on the application needs and type of devices to enable commercial consideration.

## Applications and Future Directions

Besides electricity and hydrogen production, a number of avenues have been investigated based on the bioelectrochemical approach (Fig. 3). Recovery of nutrients, such as nitrogen and phosphorous, has been demonstrated in BES systems. Production of ammonia gas at the cathode from dissolved ammonium in anode solution,[25] as well as production of struvite via precipitation of the phosphorus has been shown.[26,27] The ability to transfer electrons in the reverse direction, *i.e.*, from the cathode to microbes has also been reported, leading to the potential for bioelectrosynthesis of fuels and chemicals using biocathodes.[28] Several environmental applications have also been studied including clean-up of produced water[29] and bioremediation of pollutants. The transfer of ions between electrodes as a result of electrochemical charge separation has been employed to desalinate water. This has been coupled with energy production by BES to develop synergistic processes to clean salt and organic contaminants simultaneously.[30,31] BES systems have also been investigated as an alternative method for recovering dissolved carbon from biorefinery process water,[7,32] increasing the energy efficiency of conversion of biomass to bioenergy.

The discovery of biological nanowires and capacitive storage of electroactive biofilms has created an interest into bioelectronic applications. Research into characterization of the electronic structures of the electron transfer proteins and polymers has been initiated. The novelty of the conductive biological direct electron transfer offers a way to connect hard and soft materials, enabling electronic connectivity between silicon-type materials and biological components at the micro- and nano-scale. Development of bioelectronic devices, such as supercapacitors and transistors, has been envisioned using meta-heme cytochromes, gated proteins, etc.[33] Investigations which began a decade ago in the area of MFCs haves evolved and generated an interdisciplinary field with potential to impact a wide range of issues in the water, energy, and environment sectors in the coming decades.

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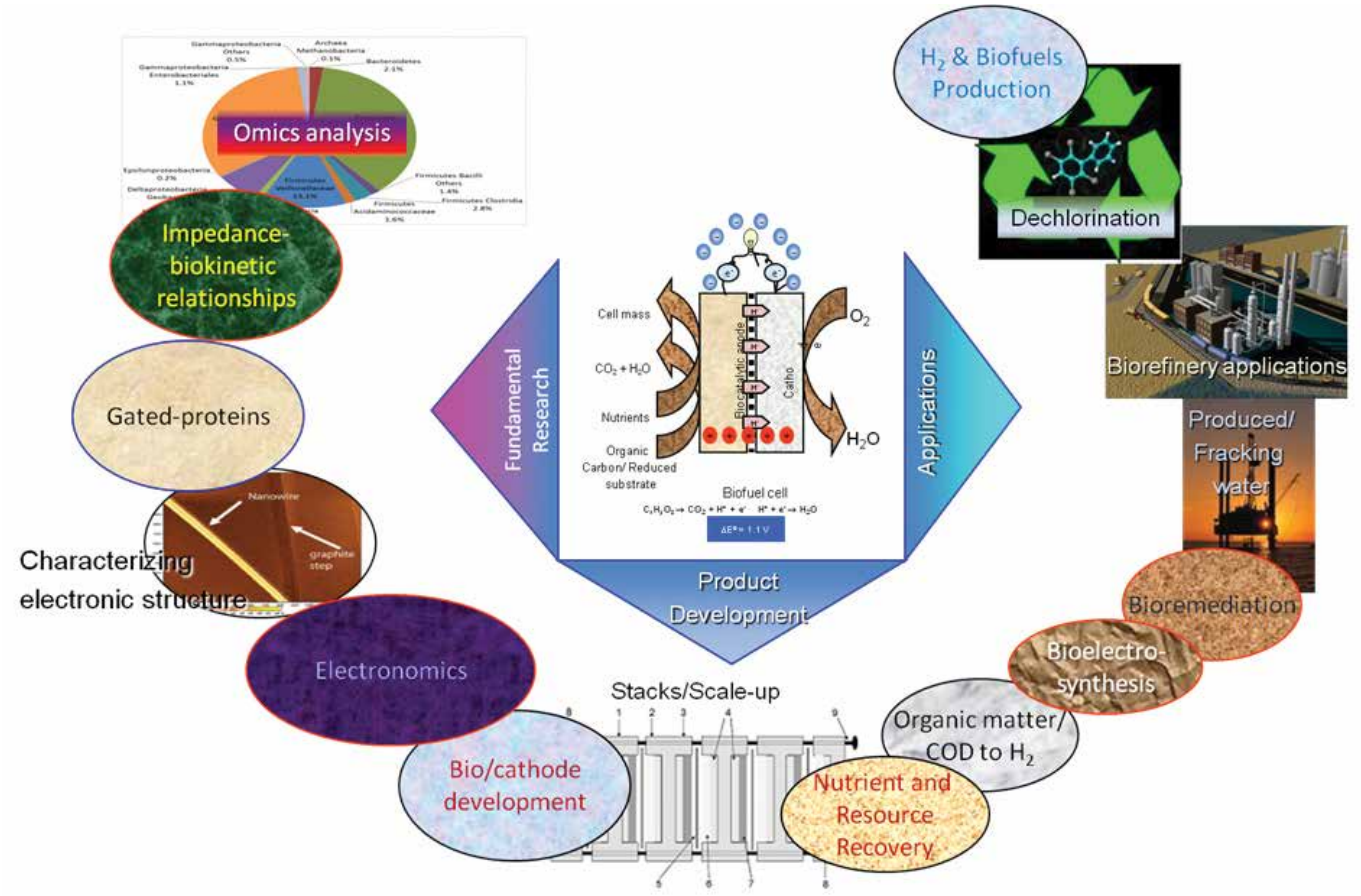


**Fig. 3.** *Potential directions for bioelectrochemical R&D and applications.*

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