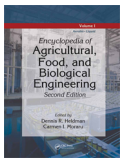

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Enzymatic and Microbial Electrochemical Systems

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Enzymatic and Microbial Electrochemical Systems

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Abstract
Enzymatic and microbial electrochemical systems (MESs) utilize the ability of biological components—enzymes and microbes—to catalyze an oxidation or reduction reaction at solid-state electrodes. A commonly known system is the microbial fuel cell in which electricity is produced via the microbially catalyzed oxidation of organic matter. The electrochemical systems that are discussed have a wide array of potential applications, including wastewater treatment, chemical production, biosensing, biocomputing, and pollution remediation. Here, we provide a background to these technologies, an overview of current research, and prospects for future development and practical application.

INTRODUCTION

Bioelectrochemical systems (BESs) utilize a biocatalyst at electrodes. Within this area, enzymatic electrochemical systems include enzymatic fuel cells (also referred to as biofuel cells), which use enzymes as biocatalysts, while microbial electrochemical systems (MESs) include microbial fuel cells (MFCs), microbial electrolysis cells (MECs), and microbial three-electrode cells (M3Cs), which utilize living microbes. Some variations in the general classification for MESs have been made with new abbreviations, such as microbial desalination cells and microbial reverse-electrodialysis electrolysis cells. Hybrids of enzymes and microbes at electrodes have also been developed. While most of these technologies are still at the laboratory scale, potential applications are diverse and include energy generation, product generation, CO_2 recovery, desalination, pollutant remediation, biocomputing, and biosensing.

ENZYMATIC FUEL CELLS

Enzymatic fuel cells utilize enzymes as the biocatalysts for the oxidation of organic substrates to produce energy. These devices consist of oxidation and reduction half-reactions occurring at two separate electrodes: the anode (oxidation) and the cathode (reduction). At the anode, the enzyme-catalyzed oxidation of organic matter (fuel) generates electrons, which are transferred to a solid-state electrode by either direct electron transfer (DET) or mediated electron transfer (MET).[1] Electrons are passed through an external circuit where they drive an electrical load before traveling to the cathode. Here, the reduction of oxygen to water, which is possibly also catalyzed by enzymes, completes the reduction half of the oxidation–reduction reaction. The specificity of the enzymes used in these cells allows the anode and cathode to exist in the same physical chamber, unlike some other types of fuel cells.[2] However, this specificity can prevent complete oxidation of the substrate, thus, limiting power output.[2]

Enzymatic fuel cells typically produce power densities that are orders of magnitude higher than MFCs; however, they are limited by the lifetime of the enzyme.[1,3] New immobilization techniques (e.g., entrapment, chemical bonding, and cross-linking) have extended the lifetime of enzyme catalysts. Furthermore, encapsulation in micellar polymers can prevent denaturing and extend lifetimes beyond a year.[1,4] Recent advances in enzyme cascades (multiple enzyme systems) have allowed for the complete oxidation of glycerol in a biofuel cell.[1,5] These multiple enzyme systems have also been shown to utilize mixed fuels, further improving the potential for application.[1] In addition, the specificity of enzymes allows for the development of multiple enzyme systems; here, multiple simultaneous reactions can occur without interference, which has led to the development of biocomputing systems for information processing.[6–8] Further advances in the development of immobilization techniques and enzyme cascades, as well as a deeper understanding of the charge transfer mechanisms, will be crucial if commercial applications of enzymatic fuel cells are to be considered.

MICROBIAL FUEL CELLS

The most extensively researched type of MESs are MFCs in which microorganisms act as catalysts for generating

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electricity from the chemical energy of organic compounds [possibly from organic materials in waste (water)].[9] An MFC consists of two electrodes that are the anode and the cathode located in their respective compartments. Stainless steel mesh and carbon in various forms, such as expanded graphite cloth, carbon cloth, and carbon paper, are the most common choices for electrode material.[10] Typically, at the MFC anode, the electron donor is an organic compound, which also fulfills the role of a carbon source for the microbial community. Bacteria oxidize this electron donor and transfer the electrons to the electrode (i.e., electron acceptor) via different mechanisms. The anode and cathode are separated by a membrane (anion or cation exchange), which isolates the two environments while still permitting ion flow for charge balance. At the cathode of MFCs, oxygen is reduced either abiotically by using appropriate catalysts (e.g., Pt catalyst on carbon) or biologically by bacteria. The use of bacteria at the cathode as catalysts is economically beneficial since otherwise expensive noble metals have to be used to overcome the high overpotential (difference between the applied potential in practice to achieve the reaction and theoretical potential as predicted from the Nernst equation) associated with oxygen reduction.[11]

Two parameters are used as performance indicators for MFCs: 1) the maximum power density (W/m^3 or W/m^2), which is calculated using a power curve, and 2) the coulombic efficiency or coulombic recovery (%), which indicates the number of coulombs being transferred as electric current either from the total coulombs present in the substrate or from the total coulombs removed from the substrate.[11] Similar to chemical batteries, MFCs can be operated in series and/or parallel configurations to maximize output.[12] In a recent life cycle assessment analysis of MFCs, it was estimated that to achieve considerable environmental benefits compared with anaerobic digestion, these devices would have to reach current densities of at least 1000 A/m^3.[13] Since MFCs present attractive options for decentralized wastewater treatment, multiple pilot-scale applications have emerged recently with limited degrees of success.[14,15]

MICROBIAL ELECTROLYSIS CELLS

In addition to MFCs, other MESs have been designed to utilize the unique ability of electrode-respiring bacteria, including MECs for which chemical products can be generated. This is achieved by using an external power supply, which applies a small voltage to drive chemical-producing reactions at the cathode.[11,16] In MECs, the anodic processes remain similar to those in MFCs; therefore, the electrons flowing into the MEC circuit can still be derived from microbial substrate oxidation at the anode. Cathodic reactions can be aerobic or anaerobic and can occur on bare electrodes, chemically catalyzed electrodes, or biocathodes (with enzymes or microbes). This flexibility opens the door to a wide variety of higher value products, including hydrogen,[17,18] methane,[19–21] ethanol,[22] 2-oxobutyrate,[23] and hydrogen peroxide.[24]

There is a large interest in the production of hydrogen in MECs as a source of renewable energy[25,26]; however, the collection of a gaseous product from the cathode chamber presents new challenges. Methane is another potential fuel source that can be generated in MECs; however, its low commercial value limits the economic feasibility. The production of ethanol requires the addition of an unsustainable redox mediator and is further limited by high overpotentials, low recovery rates (49%), and competing products (e.g., methane, hydrogen, and *n*-butyrate).[22] One study has shown the ability to convert CO_2 to small amounts of 2-oxobutyrate; this application is promising for two reasons: 1) it can be coupled to a CO_2-generating process to decrease CO_2 release to the atmosphere and 2) it produces a fuel with a higher energy density than ethanol.[23] The production of hydrogen peroxide in MECs is promising because of its high value from its use as an oxidant in paper bleaching, chemical synthesis, and textile bleaching[27]; an initial study has demonstrated the capability to produce 0.13 wt% hydrogen peroxide in a laboratory-scale MEC.[24] Another alternative to energy-based products is the production of caustic soda, a strong base comprised mainly of sodium and/or potassium hydroxide with a wide variety of industrial uses.[28] In addition, the use of MECs has been demonstrated for the remediation of 2-chlorophenol,[29] tetrachloroethene,[30] nitrate,[31,32] and uranium.[33] It is important to note that all these systems are still in the laboratory phase and their overall efficiencies and long-term reliability must be proven before they can be used for practical applications.

MICROBIAL THREE-ELECTRODE CELLS

M3Cs are based on the electrochemical half-cell and are used when either microbial oxidation or reduction with an electrode is of interest; it is used frequently for research, biosensing, and biocomputing applications. An M3C contains three electrodes (working, counter, and reference) and is controlled by a potentiostat, which is an electronic device used to control the electrochemical conditions. These three-electrode systems can be operated with or without a membrane. The potential of the working electrode (where the process of interest is occurring) is controlled against a reference electrode, while the counter electrode serves as a current drain for the cell. M3Cs can be a powerful tool for studying microbial processes and interactions in both pure and mixed cultures.[34,35] Specifically, they can be used for the identification of the most efficient microorganisms for electrode-based processes and also to screen organisms for use in MFCs and MECs. In addition, organisms have

been studied in M3Cs to determine the effects of electrode potential on overall productivity.[36] M3Cs can also be used as biosensors to monitor environmental variables, including microbial respiration and the presence of chemicals (i.e., biochemical oxygen demand and acetate), although these techniques still need to be further developed. Another application is biocomputing where biological systems transduce certain inputs signals (e.g., chemical signals) to produce digital output signals, thus, for instance, forming Boolean logic gates.[37] Both enzymatic and microbial catalysts have been used in biocomputing systems.[6,7,37] One potential application of these biosensors is smart medical devices, which would be capable of making decisions based on *in-situ* and real-time measurements. In addition, M3Cs could be used for the monitoring and control of various biological processes, such as activated sludge treatment, fermentation, and pollutant remediation. This biosensing and biocomputing area is relatively new, and further work promises to result in additional applications. The biosensing/biocomputing applications may also be possible in enzymatic electrochemical systems, MFCs, and MECs.

MECHANISMS OF ELECTRON TRANSFER

There are several known and proposed mechanisms of extracellular electron transfer (EET) between biocatalysts and electrodes. The different mechanisms have varying efficiencies and play a role in the overall performance of enzymatic systems and MESs.[38] To date, most known EET mechanisms fall into two general categories: DET and MET. This is the case for both enzymes and bacteria; below we will focus on bacterial transfer of electrons.

Within DET, the following mechanisms have been described: direct oxidation of membrane-bound *c*-type cytochromes and longer distance transfer through conductive pili. In the direct oxidation of outer membrane *c*-type cytochromes, metabolic electrons are transferred from the electron transport chain to *c*-type cytochromes on the cell surface, which in turn donate electrons directly to the solid surface.[38] Some bacteria may also use conductive pili to transport electrons directly to the electrode[39–41]; however, the specifics of this mechanism are not completely understood. Some researchers have hypothesized that pilin proteins are conductive and may be involved in oxidation/reduction reactions, while others have speculated that the pili are only structural and are covered by some other redox-active compound, possibly cytochromes.[39] Both DET mechanisms require cell attachment to the surface.

MET allows cells to transfer electrons to an electrode without direct physical contact with a soluble electron shuttle. This can occur through the use of exogenous or endogenous electron shuttles. Exogenous shuttles include methylene blue, neutral red, methyl viologen, and anthraquinone disulfonate,[38,42–44] while endogenously produced mediators include flavins, phenazines, and Quinones.[34,45] MET may sometimes utilize outer membrane *c*-type cytochromes, but detailed biological mechanisms are not yet known for all MET processes.

There are some EET mechanisms that do not fit into the categories of DET and MET, including electrokinesis (which could involve some of the previous mechanisms), redox-active membrane vesicles, and cytochrome–mediator complexes.[46–49] Electrokinesis is a process in which bacteria build up metabolic electrons and then periodically swim to and touch a solid electron acceptor for a short time to release these electrons.[48] Another mechanism that could enhance EET at a distance is membrane vesicles that act as electron shuttles. Yet another mechanism of electron transfer with cytochrome–mediator complexes, such as between cytochromes and flavins, is still being investigated in more detail.[47,49]

REFERENCES

1. Minteer, S.D.; Liaw, Y.B.; Cooney, M.J. Enzyme-based biofuel cells. Curr. Opin. Biotechnol. **2007**, *18* (3), 228–234.
2. Barton, S.C.; Gallaway, J.; Atanassov, P. Enzymatic biofuel cells for implantable and microscale devices. Chem. Rev. **2004**, *104* (10), 4867–4886.
3. Cooney, M.J.; Svoboda, V.; Lau, C.; Martin, G.; Minteer, S.D. Enzyme catalysed biofuel cells. Energy Environ. Sci. **2008**, *1* (3), 320–337.
4. Ivnitski, D.; Branch, B.; Atanassov, P.; Apblett, C. Glucose oxidase anode for biofuel cell based on direct electron transfer. Electrochem. Commun. **2006**, *8* (8), 1204–1210.
5. Minteer, S.D.; Arechederra, L.R. Complete oxidation of glycerol in an enzymatic biofuel cell. Fuel Cells **2009**, *9* (1), 63–69.
6. Katz, E. Enzyme-based biofuel cells with switchable and tunable power output. Abstr. Papers Am. Chem. Soc. **2005**, *230*, U1670–U1671.
7. Strack, G.; Pita, M.; Ornatska, M.; Katz, E. Boolean logic gates that use enzymes as input signals. Chembiochem: Eur. J. Chem. Biol. **2008**, *9* (8), 1260–1266.
8. Katz, E.; Privman, V. Enzyme-based logic systems for information processing. Chem. Soc. Rev. **2010**, *39* (5), 1835–1857.
9. Potter, M.C. Electrical effects accompanying the decomposition of organic compounds. Proc. Roy. Soc. Lond. Ser. B **1911**, *84* (571), 260–276.
10. Pant, D.; Van Bogaert, G.; Porto-Carrero, C.; Diels, L.; Vanbroekhoven, K. Anode and cathode materials characterization for a microbial fuel cell in half cell configuration. Water Sci. Technol. **2011**, *63* (10), 2457–2461.
11. Logan, B.E.; Hamelers, B.; Rozendal, R.; Schröder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K. Microbial fuel cells: Methodology and technology. Environ. Sci. Technol. **2006**, *40* (17), 5181–5192.
12. Dekker, A.; Ter Heijne, A.; Saakes, M.; Hamelers, H.V.; Buisman, C.J. Analysis and improvement of a scaled-up and stacked microbial fuel cell. Environ. Sci. Technol. **2009**, *43* (23), 9038–9042.

13. Foley, J.M.; Rozendal, A.R.; Hertle, C.K.; Lant, P.A.; Rabaey, K. Life cycle assessment of high-rate anaerobic treatment, microbial fuel cells, and microbial electrolysis cells. Environ. Sci. Technol. **2010**, *44* (9), 3629–3637.
14. Grifantini, K. Microbes for off-the-grid electricity. MIT Technology Reviews, September 4, **2008**.
15. Kalman, M. A less wasteful way to deal with wastewater. MIT Technology Reviews, July 5, **2011**.
16. Harnisch, F.; Schroder, U. From MFC to MXC: Chemical and biological cathodes and their potential for microbial bioelectrochemical systems. Chem. Soc. Rev. **2010**, *39* (11), 4433–4448.
17. Liu, H.; Grot, S.; Logan, B.E. Electrochemically assisted microbial production of hydrogen from acetate. Environ. Sci. Technol. **2005**, *39* (11), 4317–4320.
18. Rozendal, R.A.; Hamelers, H.V.M.; Euverinkb, G.J.W.; Metzb, S.J.; Buismana, C.J.N. Principle and perspectives of hydrogen production through biocatalyzed electrolysis. Int. J. Hydrogen Energy **2006**, *31* (12), 1632–1640.
19. Clauwaert, P.; Tolêdo, R.; van der Ha, D.; Crab, R.; Verstraete, W.; Hu, H.; Udert, K.M.; Rabaey, K. Combining biocatalyzed electrolysis with anaerobic digestion. Water Sci. Technol. **2008**, *57* (4), 575–579.
20. Cheng, S.A.; Xing, F.D.; Call, D.F.; Logan, B.E. Direct biological conversion of electrical current into methane by electromethanogenesis. Environ. Sci. Technol. **2009**, *43* (10), 3953–3958.
21. Villano, M.; Aulenta, F.; Beccari, M.; Majone, M. Microbial generation of H_2 or CH_4 coupled to wastewater treatment in bioelectrochemical systems. Chem. Eng. Trans. **2010**, *20*, 163–168.
22. Steinbusch, K.J.J.; Hamelers, H.V.M.; Schaap, J.D.; Kampman, C.; Buisman, C.J.N. Bioelectrochemical ethanol production through mediated acetate reduction by mixed cultures. Environ. Sci. Technol. **2010**, *44* (1), 513–517.
23. Nevin, K.P.; Woodard, L.T.; Franks, A.E.; Summers, Z.M.; Lovley, D.R. Microbial electrosynthesis: Feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic compounds. Mbio **2010**, *1* (2), e00103-10.
24. Rozendal, R.A.; Leone, E.; Keller, J.; Rabaey, K. Efficient hydrogen peroxide generation from organic matter in a bioelectrochemical system. Electrochem. Commun. **2009**, *11* (9), 1752–1755.
25. Turner, J.A. Sustainable hydrogen production. Science **2004**, *305* (5686), 972–974.
26. Hu, H.Q.; Fan, Z.Y.; Liu, H. Hydrogen production using single-chamber membrane-free microbial electrolysis cells. Water Res. **2008**, *42* (15), 4172–4178.
27. Campos-Martin, J.M.; Blanco-Brieva, G.; Fierro, J.L.G. Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. Angew. Chem. Int. Ed. **2006**, *45* (42), 6962–6984.
28. Rabaey, K.; Butzer, S.; Brown, S.; Keller, J.; Rozendal, R.A. High current generation coupled to caustic production using a lamellar bioelectrochemical system. Environ. Sci. Technol. **2010**, *44* (11), 4315–4321.
29. Strycharz, S.M.; Gannon, M.S.; Boles, A.R.; Franks, A.E.; Nevin, K.P.; Lovley, D.R. Reductive dechlorination of 2-chlorophenol by *Anaeromyxobacter dehalogenans* with an electrode serving as the electron donor. Environ. Microbiol. Rep. **2010**, *2* (2), 289–294.
30. Strycharz, S.M.; Woodard, L.T.; Johnson, J.P.; Nevin, K.P.; Sanford, R.A.; Löffler, F.E.; Lovley, D.R. Graphite electrode as a sole electron donor for reductive dechlorination of tetrachlorethene by *Geobacter lovleyi*. Appl. Environ. Microbiol. **2008**, *74* (19), 5943–5947.
31. Wang, H.Y.; Qu, H.J. Combined bioelectrochemical and sulfur autotrophic denitrification for drinking water treatment. Water Res. **2003**, *37* (15), 3767–3775.
32. Clauwaert, P.; Rabaey, K.; Aelterman, P.; de Schamphelaire, L.; Pham, T.H.; Boeckx, P.; Boon, N.; Verstraete, W. Biological denitrification in microbial fuel cells. Environ. Sci. Technol. **2007**, *41* (9), 3354–3360.
33. Gregory, K.B.; Lovley, R.D. Remediation and recovery of uranium from contaminated subsurface environments with electrodes. Environ. Sci. Technol. **2005**, *39* (22), 8943–8947.
34. Venkataraman, A.; Rosenbaum, M.; Arends, J.B.A.; Halitschke, R.; Angenent, L.T. Quorum sensing regulates electric current generation of *Pseudomonas aeruginosa* PA14 in bioelectrochemical systems. Electrochem. Commun. **2010**, *12* (3), 459–462.
35. Venkataraman, A.; Rosenbaum, M.A.; Perkins, S.D.; Werner, J.J.; Angenent, L.T. Metabolite-based mutualism between *Pseudomonas aeruginosa* PA14 and *Enterobacter aerogenes* enhances current generation in bioelectrochemical systems. Energy Environ. Sci. **2011**, *4*, 4550–4559.
36. Torres, C.I.; Krajmalnik-Brown, R.; Parameswaran, P.; Marcus, A.K.; Wanger, G.; Gorby, Y.A.; Rittmann, B.E. Selecting anode-respiring bacteria based on anode potential: Phylogenetic, electrochemical, and microscopic characterization. Environ. Sci. Technol. **2009**, *43* (24), 9519–9524.
37. Li, Z.J.; Rosenbaum, A.M.; Venkataraman, A.; Tam, T.K.; Katz, E.; Angenent, L.T. Bacteria-based AND logic gate: A decision-making and self-powered biosensor. Chem. Commun. **2011**, *47* (11), 3060–3062.
38. Schröder, U. Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency. Phys. Chem. Chem. Phys. **2007**, *9* (21), 2619–2629.
39. Reguera, G.; McCarthy, K.D.; Mehta, T.; Nicoll, J.S.; Tuominen, M.T.; Lovley, D.R. Extracellular electron transfer via microbial nanowires. Nature **2005**, *435* (7045), 1098–1101.
40. Gorby, Y.A.; Yanina, S.; McLean, J.S.; Rosso, K.M.; Moyles, D.; Dohnalkova, A.; Beveridge, T.J.; Chang, I.S.; Kim, B.H.; Kim, K.S.; Culley, D.E.; Reed, S.B.; Romine, M.F.; Saffarini, D.A.; Hill, E.A.; Shi, L.; Elias, D.A.; Kennedy, D.W.; Pinchuk, G.; Watanabe, K.; Ishii, S.; Logan, B.; Nealson, K.H.; Fredrickson, J.K. Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms. Proc. Natl. Acad. Sci. U.S.A. **2006**, 103.
41. El-Naggar, M.Y.; Wanger, G.; Leung, K.M.; Yuzvinsky, T.D.; Southam, G.; Yang, J.; Lau, W.M.; Nealson, K.H.; Gorby, Y.A. Electrical transport along bacterial nanowires from *Shewanella oneidensis* MR-1. Proc. Natl. Acad. Sci. U.S.A. **2010**, *107* (42), 18127–18131.

42. Park, D.H.; Zeikus, G.J. Electricity generation in microbial fuel cells using neutral red as an electronophore. Appl. Environ. Microbiol. **2000**, *66* (4), 1292–1297.
43. Ringeisen, B.R.; Henderson, E.; Wu, P.K.; Pietron, J.; Ray, R.; Little, B.; Biffinger, J.C.; Jones-Meehan, J.M. High power density from a miniature microbial fuel cell using *Shewanella oneidensis* DSP10. Environ. Sci. Technol. **2006**, *40* (8), 2629–2634.
44. Aulenta, F.; Catervi, A.; Majone, M.; Panero, S.; Reale, P.; Rossetti, S. Electron transfer from a solid-state electrode assisted by methyl viologen sustains efficient microbial reductive dechlorination of TCE. Environ. Sci. Technol. **2007**, *41* (7), 2554–2559.
45. Marsili, E.; Baron, B.D.; Shikhare, I.D.; Coursolle, D.; Gralnick, J.A.; Bond, D.R. *Shewanella* secretes flavins that mediate extracellular electron transfer. Proc. Natl. Acad. Sci. U.S.A. **2008**, *105* (10), 3968–3973.
46. Gorby, Y.; Mclean, J.; Korenevsky, A.A.; Rosso, K.M.; El-Naggar, M.Y.; Beveridge, T.J. Redox-reactive membrane vesicles produced by *Shewanella*. Geobiology **2008**, *6* (3), 232–241.
47. Okamoto, A.; Nakamura, R.; Ishii, K.; Hashimoto, K. In vivo electrochemistry of c-type cytochrome-mediated electron-transfer with chemical marking. Chembiochem: Eur. J. Chem. Biol. **2009**, *10* (14), 2329–2332.
48. Harris, H.W.; El-Naggar, M.Y.; Bretschger, O.; Ward, M.J.; Romine, M.F.; Obraztsova, A.Y.; Nealson, K.H. Electrokinesis is a microbial behavior that requires extracellular electron transport. Proc. Natl. Acad. Sci. U.S.A. **2010**, *107* (1), 326–331.
49. Okamoto, A.; Nakamura, R.; Hashimoto, K. In-vivo identification of direct electron transfer from *Shewanella oneidensis* MR-1 to electrodes via outer-membrane OmcA-MtrCAB protein complexes. Electrochim. Acta **2011**, *56* (16), 5526–5531.