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51. Water productivity P is defined as the value of goods and services V generated per unit of water used Q: $P = V/Q$. The percent change in potable water productivity associated with the implementation of a water-saving scheme is $\Delta\overline{P} \equiv 100(P_2 - P_1)/P_1$, where P_1 and P_2 represent the productivity of potable water before and after the scheme is implemented (not all water-saving schemes discussed in the text directly reduced potable water use, but for consistency across the 21 case studies, water savings were benchmarked relative to potable water use at the appropriate scale). Assuming that the water-saving scheme does not change the value of goods and services produced, $\Delta\overline{P}$ can be calculated directly from potable (municipal) water use before (Q_1) and after (Q_2) scheme implementation: $\Delta\overline{P} = 100(Q_1/Q_2 - 1)$.

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REVIEW

Conversion of Wastes into Bioelectricity and Chemicals by Using Microbial Electrochemical Technologies

Bruce E. Logan[1]* and Korneel Rabaey[2]

Waste biomass is a cheap and relatively abundant source of electrons for microbes capable of producing electrical current outside the cell. Rapidly developing microbial electrochemical technologies, such as microbial fuel cells, are part of a diverse platform of future sustainable energy and chemical production technologies. We review the key advances that will enable the use of exoelectrogenic microorganisms to generate biofuels, hydrogen gas, methane, and other valuable inorganic and organic chemicals. Moreover, we examine the key challenges for implementing these systems and compare them to similar renewable energy technologies. Although commercial development is already underway in several different applications, ranging from wastewater treatment to industrial chemical production, further research is needed regarding efficiency, scalability, system lifetimes, and reliability.

There is substantial energy in organic matter that is currently wasted or lost in treatment processes. Treatment of organic-rich wastewater currently consumes about 15 GW, or about 3% of all electrical power produced in the United States (*1*), but domestic, industrial, and animal wastewater together contain ~1.5×10^{11} kilowatt-hour (kWh) of potential energy (~17 GW of power) (*2*). Capturing part of this energy would provide a new source of electrical power that would also avoid the consumption of energy for wastewater treatment. Furthermore, agricultural practices could be modified to annually produce an additional 1.34 billion tons of biomass for energy production, without affecting food production (*3*), which is equivalent to more than 600 GW of continuous power. These different sources of waste organic matter can be a rich resource for energy production if we can develop cost-effective methods for harnessing this energy. Alternatively, we could capture this waste biomass energy in industrial processes to make other useful chemicals, such as biofuels or industrial chemicals, that currently require electricity or organic substrates for this purpose.

Recently developed microbial electrochemical technologies (METs) that use microorganisms to catalyze different electrochemical reactions, such as microbial fuel cells (MFCs) that generated electrical power, are promising approaches for capturing the energy in waste biomass for diverse purposes. Energy production by electrochemical processes or conventional combustion requires a fuel to provide electrons and an electron acceptor (oxidizer). In METs, organic matter is the fuel, and oxygen is the primary oxidizer for aerobic respiration by bacteria. However, many other soluble chemical species can serve as oxidizers for anaerobic bacteria, including nitrate, sulfate, and carbon dioxide. Bacteria known as exoelectrogens have the ability to transfer electrons outside the cell to insoluble electron acceptors, such as iron and other metal oxides, or to electrodes in bioelectrochemical systems. The most commonly studied microorganisms are various *Geobacter* and *Shewanella* spp., but many other bacteria have been found to possess exoelectrogenic abilities (*4*). Electrons are transferred by these bacteria outside the cell indirectly, by using electron shuttles such as flavins and phenazines (*5*–*7*), or directly by using outer membrane proteins (*8*). These mechanisms can occur in combination with self-produced conductive pili called nanowires (*9*, *10*). In contrast, electrotrophic microorganisms can directly or indirectly accept electrons into the cell (*11*).

How Do Microorganisms Generate Electricity from Organic Matter?

The use of exoelectrogenic microorganisms in MFCs allows electrical power generation from nearly any source of biodegradable organic or inorganic matter in water that does not directly require oxygen as a part of the degradation process. These organic sources include simple molecules such as acetate, ethanol, glucose, and hydrogen gas; polymers such as polysaccharides, proteins, and cellulose; and many types of wastewaters from domestic, food processing, and animal sources (*12*, *13*) (Fig. 1). In an MFC, bacteria release electrons to the anode and protons into solution, resulting in a negative anode potential of about −0.2 V (versus a standard hydrogen electrode) that is generally only slightly more positive than that of the half-cell reaction for the substrate (e.g., a midpoint potential at pH = 7 of −0.28 V for acetate) (*14*). In most cases, oxygen in air is used as a sustainable oxidizer at the cathode, with a typical maximum potential of +0.3 V, producing an overall maximum cell potential of +0.5 V. Cathode potentials obtained in MFCs are considerably lower than theoretical values (~+0.8 V, with oxygen) even with Pt-catalyzed cathodes (*15*, *16*) (Fig. 1). One of the most promising nonprecious metal materials used for oxygen reduction in MFCs is activated carbon, because it is both inexpensive and renewably produced from waste biomass (*17*). Nitrate is an alternate electron acceptor that produces comparable cell voltages because of its high solubility relative to oxygen (*18*). Voltages cannot be increased by linking MFCs in series as is done with batteries (*19*, *20*). However, higher voltages can be captured from arrays of MFCs by wiring them to charge capacitors in parallel and then discharging the capacitors in series, resulting in nearly additive voltages from the individual MFCs (*21*).

The power densities produced by MFCs are lower than those possible by using hydrogen fuel cells because of high internal resistances, the limited temperature and solution conditions tolerated by microorganisms, substrate degradability, and biofilm kinetics. Hydrogen fuel cells use an ion-exchange membrane as a solid electrolyte for charge transfer. Membranes are not required in MFCs, and using a membrane between the anode and cathode can add internal resistance, which will

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reduce power (*15*). Instead of using ion-conductive membranes, many MFCs are being designed with separators or coatings on the cathode to insulate the cathode and protect it from biofilm growth (*22*). Water serves as the electrolyte for charge transfer in an MFC, with power increased in proportion to solution conductivity up to limits tolerated by bacteria. Charge transfer is different from a hydrogen fuel cell because charge is balanced primarily by ions more abundant in the water than protons, such as sodium and potassium. This results in pH gradients that can reduce performance (*23*, *24*), although in some instances pH changes can be useful, as discussed below. Typical maximum power densities in MFCs are ~2 to 3 W m^{-2} of projected electrode (usually the cathode), under optimum conditions of ~30°C, solution conductivities of ~20 mS cm^{-1}, and well-buffered solutions at neutral or slightly alkaline pH. MFC power densities are much lower than those in hydrogen fuel cells, which produce on the order of 1 W cm^{-2}, but these power densities are consistent with chemical fluxes into biofilms based on an analogous flux in terms of equivalent electrons (for example, 24 mol e^- per mol glucose) (*14*). Upper limits of 17 to 19 W m^{-2} have been predicted for MFCs on the basis of estimates assuming minimal internal resistance or by assuming first-order kinetics typical of microorganisms in biofilms (*4*, *25*). Increasing electrode-packing densities (electrode area per volume of reactor) has produced up to 1.55 kW per m^3 of reactor volume (2.77 W m^{-2}) under optimum conditions (*26*), which is much higher than typically produced from wastewaters (<0.5 W m^{-2}) (*27*, *28*). Lower power densities obtained with wastewaters are due to slower biodegradation kinetics for complex substrates, lower solution conductivities, and reduced buffer capacities.

The complex nature of many waste biomass sources requires a diverse microbial community to degrade the various components of the organic matter. Although many bacteria may produce electrical current, high power densities from complex sources of organic matter are typically associated with the presence of *Geobacteraceae* in the anodic community (*4*, *29*). These microbes use a limited number of substrates, with acetate being the most common among different strains, although lactate and a few others are also possible substrates (*30*, *31*). Syntrophic interactions can therefore be required to break down complex organic matter into simpler substrates that can be used by exoelectrogens (Fig. 1) (*29*). The nature of the syntrophic associations is highly similar to anaerobic digestion, where diverse substrates are broken down to simple molecules that are used for methane generation by members of the *Methanosarcinales* genus (*32*). Community associations are not yet well understood in MFCs, with certain microbes affecting power disproportionate to individual contributions (*33*). For example, power was increased by 30 to 70% by adding Gram-positive *Enterococcus faecium* to cultures of Gram-negative *Pseudomonas aeruginosa*, even though pure cultures of *E. faecium* produced little power (*34*). Further studies demonstrated that *Enterococcus aerogenes* could produce 2,3-butanediol, leading to increased production of an electron shuttle (phenazine) by *P. aeruginosa* (*35*).

What Types of Harvestable Chemicals Can Microorganisms Produce in Bioelectrochemical Systems?

Applying electrical power to a bioelectrochemical system can enable the generation of many different chemical products from biomass, such as biofuels (*36*). This modification is commonly referred to as a microbial electrolysis cell (MEC), based on the first systems that produced hydrogen gas through the electrolysis of biomass by bacteria as opposed to water electrolysis. Energy is added into an MEC by either using an external power source or setting an electrode potential using potentiostat. Hydrogen gas can be produced at the cathode at a theoretical potential of –0.41 V under standard conditions and neutral pH (*36*). Acetate oxidation by microorganisms could achieve an anode potential down to –0.28 V, so a minimum of –0.13 V theoretically needs to be added into the system. This voltage is much less than that needed to split water (–1.2 V) because of the favorable thermodynamics of organic matter degradation compared with the energy-demanding reaction for splitting water. Typically more negative voltages than –0.3 V are used, even with Pt catalysts, to increase gas production rates. Applied voltages down to about –1 V allow more energy to be captured in the hydrogen gas produced than the electrical energy used. However, energy efficiency is only part of the cost of producing hydrogen gas, and higher voltages may be used to make gas production cost effective.

Microorganisms can be used on the cathode to directly (via electron transfer) or indirectly (through evolved chemicals) catalyze the production of inorganic chemicals. Electrotrophic microbes are not true catalysts because they derive energy from this process. The first biocathodes used to produce methane required mediators (*37*) or hydrogen gas (*38*), but later it was shown that methanogenic communities could directly accept electrons from the cathode (*39*). Methane is commonly produced in MECs, primarily from hydrogen gas evolved from the cathode but also through acetoclastic methanogenesis (*38*, *40*). Although only a small amount of H_2 gas is typically lost in small single-chamber laboratory MECs (*41*), methanogenesis can eliminate hydrogen gas recovery in larger systems (*42*, *43*) unless the gas produced at the cathode is kept separate from methanogens (*44*). Hydrogen gas can be produced using biocathodes (*45*), although the energy efficiencies are lower

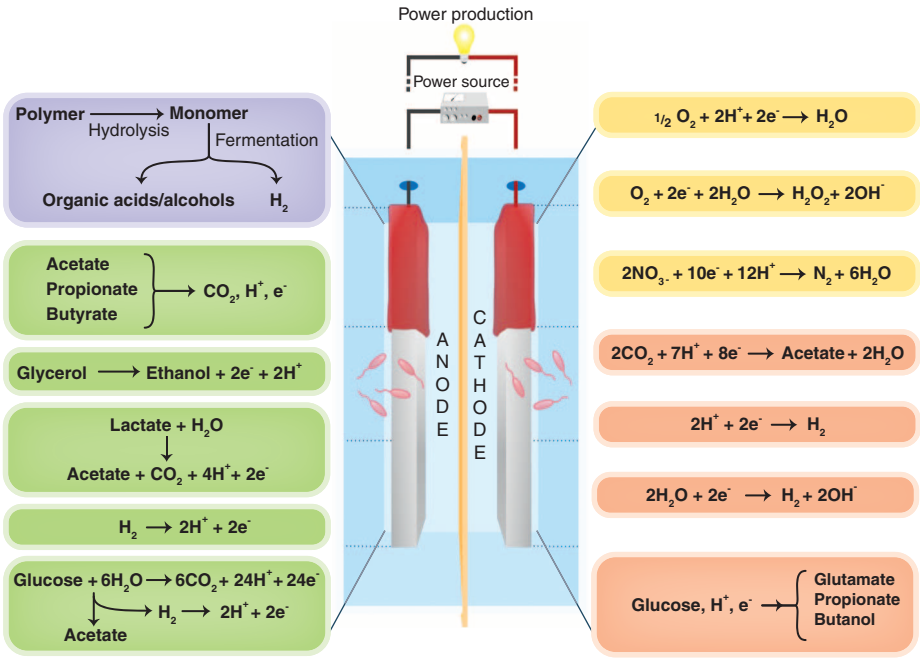

Fig. 1. Overview of anodic and cathodic reactions in a bioelectrochemical system. Electrode reactions are due to planktonic or biofilm cells or in some cases are directly electrochemically catalyzed. At the anode, polymeric material can be degraded to simple molecules, such as fatty acids and hydrogen, which can be used for current generation. Other bioconversion reactions, such as conversion of glycerol to ethanol, can also produce compounds for current generation. At the cathode, reactions can result in power generation or additional product formation. Purple indicates reactions that do not directly result in current generation; green, reactions that can produce current; yellow, reactions that can occur spontaneously or can be accelerated by adding additional power; orange, power addition is required. The stoichiometry of the reactions is principally theoretical because many conversions lead to side products as well as biomass formation.

than those of inorganic catalysts. Although a kilogram of methane has lower energy and economic value than the same mass of H_2, the complete conversion of H_2 gas evolved in an MEC to methane can still produce a positive energy balance (*43*). The gas is also enriched in methane (86%) compared with an anaerobic digester because of the consumption of carbon dioxide.

The cathodic production of hydrogen peroxide or caustic solutions appears to be a promising application of MECs (Fig. 2). When a cation-exchange membrane is placed between the anode and cathode, pH gradients rapidly develop in the two chambers, even with mildly buffered solutions (*23*). This situation can be exploited to produce NaOH concentrations as high as ~ 1 mol l^{-1} in the cathode (*46*). Production of the caustic in an industrial setting avoids purchasing a high-cost concentrated solution and the need to transport these solutions to the site. Oxygen reduction at the cathode normally produces water, but, in the absence of an efficient catalyst such as Pt, the reaction results in a two-electron transfer and the production of hydrogen peroxide (*47*). An alkaline solution of hydrogen peroxide is a strong oxidant that can be used industrially for bleaching. A life-cycle analysis suggests that production of hydrogen peroxide in MECs is more sustainable than presently used routes (*48*).

MECs can also produce a variety of organic chemicals by electroautotrophic processes using CO_2 or from substrate organics via microbial electrosynthesis (MES) (*49*). Acetate and oxo-butyrate were produced by using a culture of *Sporomusa ovata* attached to a cathode that was the sole electron donor (*50*). Although multiple homoacetogenic cultures have now shown the ability to catalyze CO_2 reduction by using electricity as donor (*51*), thus far the rates and titers produced are very low. Major improvements in production rates will be essential to bring about microbial electrosynthesis based on CO_2 for large-scale applications. For several decades, it has been known that providing reducing power to fermenting cultures with use of electrochemical processes can redirect glucose fermentations toward glutamate, butanol, and propionate (*52*–*54*). The known exoelectrogen, *Shewanella oneidensis* MR-1, was engineered to oxidize glycerol to ethanol by discharging excess reducing equivalents to the anode (*55*). Acetate was converted to ethanol by using a microbial population in an MEC (*56*). Advantages of starting from waste organics are the lower electron requirement relative to CO_2 as well as the possibility to upgrade or treat a waste stream.

How Do METs Measure Up Against Conventional Technologies for Wastewater Treatment?

Current wastewater treatment processes have their bases in processes developed over a hundred years ago, and, although there have been incremental advances, new paradigm-changing approaches are needed to enable substantial energy recovery. Treatment of domestic wastewater in a conventional activated sludge process requires –0.3 kWh m^{-3} for aeration, with about twice that used overall for pumping and in other processes (*1*). Membrane bioreactors that can achieve efficient treatment and excellent water quality are being used more frequently, but they have high energy demands (–1 to –2 kWh m^{-3}). Some wastewater treatment plants using activated sludge bioreactors have become energy neutral through the combination of nutrient removal with anaerobic digestion of sludge that produces biogas (methane) (*57*). Principal limitations of anaerobic digestion as the main treatment process (i.e., replacing activated sludge) are the need for a concentrated waste stream (>3 kg organic matter per m^3) and warmer temperatures (>20°C), and the process is only economical by using very large digesters. For these reasons, anaerobic digesters have only been used in conventional treatment plants for treatment of the sludge and not the main flow.

The strength of METs is their applicability to directly treat the wastewater while substantially decreasing the need for sludge handling and treatment resulting from low solids production. In theory, the direct generation of electricity in METs can be similar to conventional fuel cells and lead to very high energy efficiencies because they do not have Carnot cycle limitations inherent in combustion processes. However, energy recovery in METs to date have been low, leading some to question whether they can ever compete with conventional processes (*1*). The maximum power densities produced in MFCs using domestic wastewater alone (without other energy sources) have reached 12 W m^{-3} (*27*), equivalent to 0.07 kWh m^{-3} produced over 6 hours (comparable to activated sludge treatment times). This energy recovery is low considering that domestic wastewater contains ~2 kWh m^{-3} (*58*).

A more feasible role for wastewater is as an energy source for chemical production in METs, with the bulk of the treatment accomplished by using more conventional processes. By producing chemicals such as H_2 and hydrogen peroxide from wastewater instead of through electrolysis or other means, the energy contained in the organic matter is used to supply at least part of the production energy. As shown by Foley *et al.* (*48*) in a life-cycle analysis comparing anaerobic digestion, MFCs, and MECs, on-site production of chemicals can bring about a considerable environmental benefit to the overall treatment process. It is therefore important to consider whether the primary goal of using wastewater in METs is complete treatment or instead the production of useful chemicals as a part of treatment.

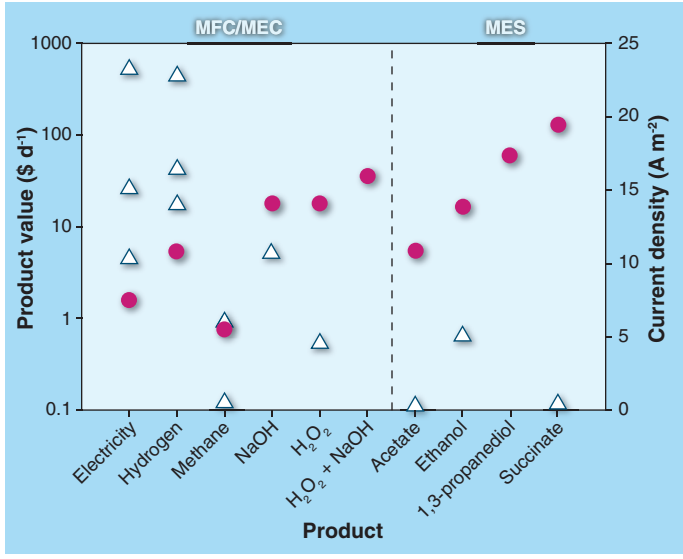

Fig. 2. Possible outcomes using different microbial electrochemical technologies in terms of economic values (calculated for 1 day at 1000 A and neglecting the cost of input materials) and current densities (exemplary for state of the art). There is roughly an inverse relationship between the value of these products (triangles) and the current densities (circles), which is in part due to the more effort in producing the lower-value products such as electricity and biofuel gases (hydrogen and methane). Generating 1000 A translates to a theoretical consumption of 7.16 kg waste organic matter (expressed as chemical oxygen demand).

Combining METs with Other Emerging Renewable Energy Technologies

Reverse electrodialysis (RED) is a process that can be used to directly create electrical power from a salinity gradient (*59*). The flow of seawater and freshwater (or treated wastewater) through pairs of ion-exchange membranes in a RED stack creates an electrical potential of 0.1 to 0.2 V per pair of membranes. Globally, up to 980 GW of power could be harvested from salinity gradient energy where freshwater flows into the sea (*60*). A RED stack can be placed between the anode and cathode chambers of an MFC or MEC, creating a hybrid technology called a microbial reverse electrodialysis cell (MRC). The favorable anode reaction provided by exoelectrogenic bacteria degrading organic matter allows MRCs with oxygen reduction at the cathode to produce three times the voltage (1.2 V) and 6.1 times the power (4.3 W m^{-2}) of an MFC lacking the membrane stack with NaCl solutions (*61*). The use of the RED stack in an MEC produced H_2 gas at energy efficiency of

up to 65%, without the need for electrical grid energy (*62*). Low-grade waste heat can be used to generate salinity gradients (high and low concentrations of salt solutions) from thermolytic chemicals such as ammonium bicarbonate (*63*). MRCs using ammonium bicarbonate have produced 3 W m^{-2} (4.5 a.m.$^{-2}$) with domestic wastewater and 5.6 W m^{-2} with acetate (30% energy efficiency, not including distillation energy) (*64*). Thermolytic solutions enable the use of MRCs at any location where there is wastewater or waste biomass and waste heat. The use of thermolytic solutions also minimizes biofouling of the membranes, which is problematic when using seawater and river water.

What Are the Prospects for Scaling Up and Commercialization?

MFCs and MECs are exciting but nascent technologies, with many opportunities and challenges for successful applications. One key factor for commercial success of these technologies will likely be lowering the cost of electrodes and associated materials to enable recovery of capital costs within only a few years. The electrodes need to have high surface areas and be tightly packed together to maximize power volumetric densities, while at the same time allowing a complex interaction of microorganisms with the wastewater (Fig. 3). Rising costs for producing electrical power coupled with incentives for carbon-neutral processes could bring these systems into practice, with sufficient investment, in the near future.

Several companies are now in the process of commercializing MFCs and MECs for various applications, including wastewater treatment and the production of biochemicals, caustic solutions, and hydrogen peroxide solutions. The main challenge of using MFCs as a stand-alone method for electrical power generation is the low value of electricity. For the same reason, it may be difficult to realize a profit on investment by using MFCs as a stand-alone method of wastewater treatment because of little profit that can be made from producing electricity. The primary economic benefit for wastewater treatment is reducing, or completely avoiding, the need for electrical power consumption for aeration. METs offer many more opportunities for novel applications than other processes such as anaerobic digestion, which do not require wastewater aeration, because they can be used to produce many different products. Although biochemical production offers additional economic incentives, the need for high current densities when making a product could preclude result in effluent organic matter concentrations that are above those allowable for direct discharge. The integration of METs into domestic and industrial sites will therefore require careful consideration of the specific opportunities at different sites and the costs involved in partial or full treatment with this bioelectrochemical approach. The overall benefits to be realized from METs provide great incentives for continued innovations, developments, and applications such as energy and chemical production from waste biomass.

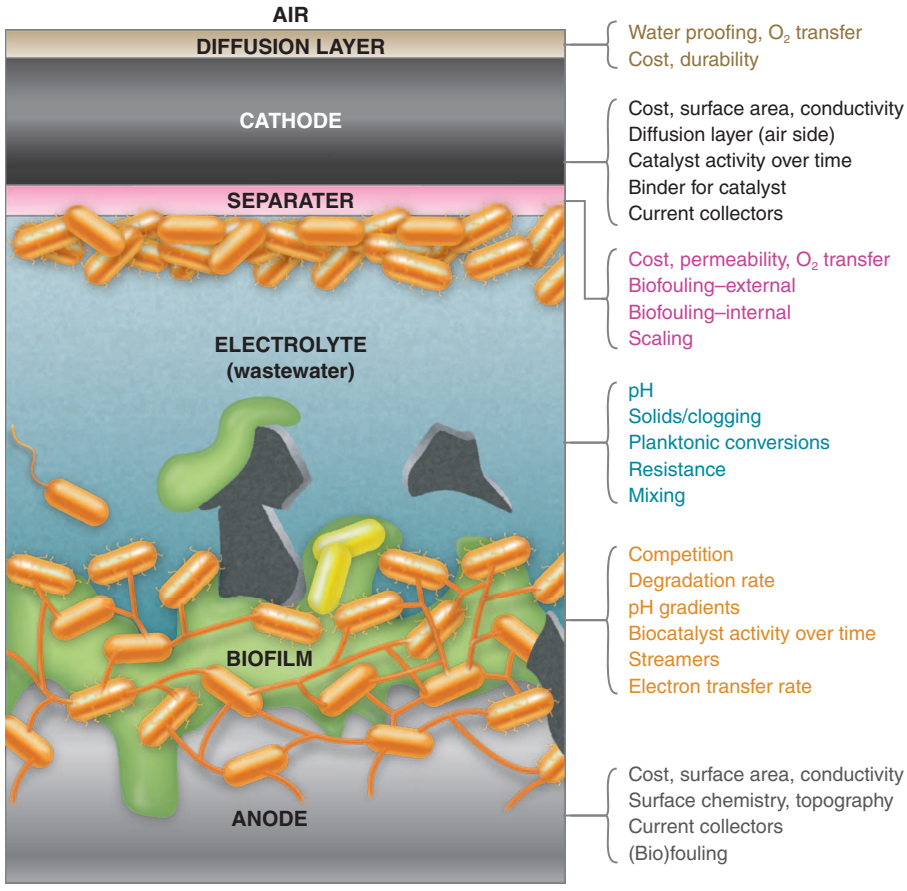

Fig. 3. The complex environment of the MFC presents many opportunities for scientific study as well as challenges for commercial applications. An electrogenic biofilm colonizes the anode, and its development depends on the specific electrode materials and properties. Within the biofilm, inert material (solids or dead cells, dark gray) can limit access for the cells to the electrode. Electroactive cells (orange) can be in direct or indirect contact with the electrode; competing cells (yellow, e.g., methanogens) do not require this contact and can thus have a competitive advantage outside of the biofilm. pH gradients can build up in the biofilm and bulk solution (electrolyte), leading to decreased performance and loss of electrochemical potential. Solids in the wastewater can lead to clogging, and planktonic cells may show competitive behavior for organic matter with the biofilm. Protons (anode) or hydroxyl ions (cathode) generated at the electrodes need to be transported to the counterelectrode, and competition with other more-abundant ions (such as sodium and chloride) can lead to changes in the bulk pH, which in turn affects the process. The cathode will catalyze oxygen reduction, but it can foul with bacteria and organic and inorganic matter, leading to reduction in catalysis. Oxygen can leak through the cathode and separator, resulting in loss of organic matter and decreased power.

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REVIEW

Challenges in Metal Recycling

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Metals are infinitely recyclable in principle, but in practice, recycling is often inefficient or essentially nonexistent because of limits imposed by social behavior, product design, recycling technologies, and the thermodynamics of separation. We review these topics, distinguishing among common, specialty, and precious metals. The most beneficial actions that could improve recycling rates are increased collection rates of discarded products, improved design for recycling, and the enhanced deployment of modern recycling methodology. As a global society, we are currently far away from a closed-loop material system. Much improvement is possible, but limitations of many kinds—not all of them technological—will preclude complete closure of the materials cycle.

The generation now between the ages of 20 and 30 is, in many parts of the world, the first to have grown up with the recycling bin as a normal part of life. Discarded paper, cans, and bottles have designated places to go, and often go there. The situation is less certain for products used for a number of years before being discarded—computers, refrigerators, automobiles—for which recycling procedures have been diverse and sporadic. And few know what happens to obsolete equipment used on behalf of individuals but owned by corporations or organizations—medical imaging machines, aircraft engines, and the like.

The recycling of products in the "occasionally discarded" or "owned by somebody else" categories is complicated by the rapid expansion of the designer's materials palette that has taken place in the past several decades (*1*, *2*). Today, virtually every stable element in the periodic table is used so as to take advantage of its unique physical and chemical properties. The result is that many products are more functional and reliable than before. An unintended consequence is that recycling has become much more complicated and challenging.

Several reviews of metal recycling have appeared in recent years (*3*–*5*). They discuss central issues such as recycling technologies, economic limitations, and methods of enhancement. Some open questions still remain: How much is going on, and what are the trends? What are its limits? Is a closed-loop materials economy possible? It is these systems-level topics that are the focus of the present work.

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The Current Status of Metal Recycling

How well is the world doing at recycling the diverse mix of elements in modern products? Two metrics answer this question best: recycled content and end-of-life recycling rate (EOL-RR). Recycled content describes the share of scrap in metal production, which is important to get a sense of the magnitude of secondary supply. This indicator, however, has two limitations. First, lifetimes of metal-containing products often span several decades, which, in combination with rapid growth in metal use, means that recycled metal flows will meet only a modest portion of demand for many years to come. Second, it does not distinguish between new (yield loss from fabrication and manufacturing) and old (postconsumer) scrap as input material, making it vulnerable to artificially increased rates based solely on preconsumer sources (fabricators may be given incentives to increase their scrap output to meet secondary demand, making recycled content an incentive for inefficiencies in fabrication and manufacturing). What recycled content means to encourage, instead, is the amount of old scrap that is collected and processed for recycling [also expressed as old scrap ratio (*6*)]. The indicator that measures this more directly is the EOL-RR, defined as the fraction of metal in discarded products that is reused in such a way as to retain its functional properties.

The EOL-RR depends on the collection rate of end-of-life products and the efficiency of the subsequent separation and pre-processing steps, all involving complex interactions of a wide variety of players (*7*). A United Nations panel recently defined and quantified recycling rates for 60 elements (Fig. 1) (*8*). Two messages jump out at once from the figure. The first is that EOL-RRs for the commonly used "base metals" (iron, copper, zinc, etc.) are above 50% (although, as the report is careful to point out, usually not very far above 50%). The second, and striking, impression

ERRATUM

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Reviews: "Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies," by B. E. Logan and K. Rabaey (10 August 2012, p. 686). In the Fig. 2 legend, the symbols should have been identified as follows: "There is roughly an inverse relationship between the value of these products (circles) and the current densities (triangles)...." On p. 689, "4.5 a.m.$^{-2}$" should have been written as "4.5 A m^{-2}." The authors also wish to thank T. Lacoere and J. Desloover for assistance in preparing the draft figures and funding from the Commonwealth Scientific and Industrial Research Organization Flagship cluster "Biotechnological solutions to Australia's transport energy and greenhouse gas challenges." The HTML version online has been corrected.