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Electrobiocommodities: powering microbial production of fuels and commodity chemicals from carbon dioxide with electricity

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Electricity can be an energy source for microbially catalyzed production of fuels and other organic commodities from carbon dioxide. These electrobiocommodities (E-BCs) can be produced directly via electrode-to-microbe electron transfer or indirectly with electrochemically generated electron donors such as H_2 or formate. Producing E-BCs may be a more efficient and environmentally sustainable strategy for converting solar energy to biocommodities than approaches that rely on biological photosynthesis. A diversity of microbial physiologies could potentially be adapted for E-BC production, but to date acetogenic microorganisms are the only organisms shown to covert electrically generated low potential electrons and carbon dioxide into multi-carbon organic products with high recovery of electrons in product. Substantial research and development will be required for E-BC commercialization.

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Introduction

Electrobiocommodities (E-BCs) are fuels or other organic commodities that microorganisms produce from carbon dioxide with the aid of electrical energy. The expected movement from an oil economy to an electric economy [1] is increasingly focusing attention on E-BCs.

When powered with solar technologies the production of E-BCs can be an artificial form of photosynthesis, proceeding via the same overall reaction as biological photosynthesis in which carbon dioxide and water are converted to organic compounds with oxygen as a byproduct [2,3]. However, E-BC production has the potential to be much more efficient in converting solar energy and carbon dioxide to desired products and to be more environmentally sustainable. For example, in one E-BC strategy, known as microbial electrosynthesis [4••,5], microbial biofilms growing on electrodes directly accept electrons from electrodes for the reduction of carbon dioxide to organic products that are excreted from the cells. This is more efficient than processes based on biological photosynthesis. One reason for this is that solar technologies are more effective in capturing solar energy than biological photosynthesis [6]. Furthermore, direct production and excretion of desired organic products with microbial electrosynthesis alleviates the need for the additional energy and water inputs as well as the waste generation associated with processing biomass to products [2,3]. Additional advantages are that E-BC processes do not compete with food production for high quality land, require a much smaller land area than biomass production, are feasible in extreme and remote environments inhospitable for intensive biomass production, and avoid the extensive environmental degradation associated with intensive production of biomass [2,7].

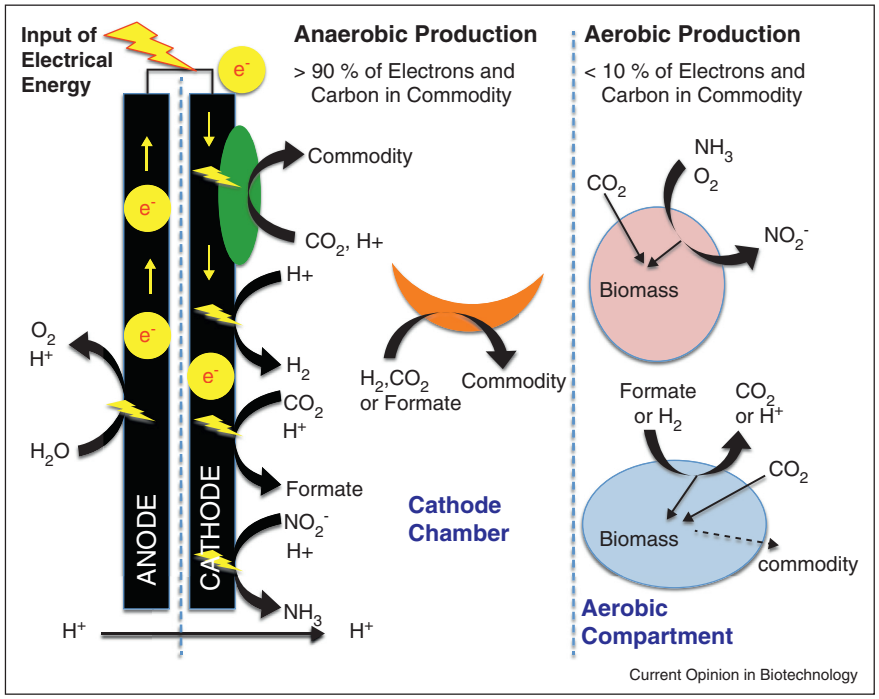
E-BC production is a subset of a broader growing interest in producing fuels and chemicals via autotrophic microbial processes [8••,9••]. For example, limitations on speed and efficiency of converting complex biomass to simpler precursors that can be biologically converted into fuels and commodities suggest that a more effective strategy may be to generate syngas from organic material, followed by microbial conversion of the syngas to desired products [10,11]. Research in the area of syngas fermentations is also applicable to E-BC production because syngas microorganisms may also be good E-BC catalysts.

This review summarizes some of the most recent concepts for powering microbial production of fuels and other organic commodities with electrical energy and research into the development and optimization of this approach.

Feeding microorganisms electrons with electrical energy

There are several ways that electrical energy can be used to provide microbes with low-potential electrons that can power microbial reduction of carbon dioxide as well as cell growth and maintenance (Figure 1). As previously reviewed [2,12], early studies employed organic molecules, such as neutral red that can function as electron shuttles, accepting electrons from electrodes and then donating electrons to electron carriers in the cell. However, this approach is less favored now because of the added cost, chemical instability, and toxicity of some of the most effective organic shuttles, as well as the complications their presence adds to recovering organic products.

Figure 1



Schematic of approaches to microbial production of organic commodities from carbon dioxide with electrical energy. Electrons are derived from water at the anode as shown, or in special cases may be derived from reduced sulfur or organic wastes. Electrical energy is applied to lower the potential of the electrons delivered at the cathode. Microorganisms capable of microbial electrosynthesis can directly accept electrons from the cathode for the reduction of carbon dioxide to organic products that are excreted from the cell. Alternatively, the appropriate electron acceptors can be abiotically reduced at the anode surface to produce H_2, formate, or ammonia. H_2 or formate can serve as electron donors for anaerobic carbon dioxide reduction to excreted organic products. Aerobic processes must be shielded from the cathode to prevent reduction of oxygen, which wastes electrons and generates reactive oxygen species that are toxic to microbes. Major constituents are shown but stoichiometrically balanced reactions are not provided.

Another possibility is to electrochemically generate traditional electron donors for microbial respiration such as H_2, formate, ammonia, sulfide, or Fe(II) [7,13•,14•]. The redox potential of H_2 and formate is low enough for microorganisms to gain energy to support growth from the direct reduction of carbon dioxide to organic compounds that are useful fuels or commodities (Figure 1). In contrast, other potential electron donors such as ammonia, sulfide, and Fe(II) require an electron acceptor, such as oxygen, with a potential higher than that of carbon dioxide to support cell growth, which as described below, can add inefficiencies and require physical separation between the site of electrochemical electron donor generation and microbial electron donor consumption.

Alternatively, electrons can be directly provided to microorganisms, known as electrotrophs [2], which can couple direct electron consumption to the reduction of carbon dioxide [4••,5]. This is potentially the most direct and efficient strategy for producing biocommodities with electrical energy. However, this is a relatively new concept [4••] and is in the infancy of development.

Water is the most abundant, inexpensive potential source of electrons for producing E-BCs. Sulfide and organic wastes are potential alternatives and have the advantage that electrons can be recovered at a lower potential, requiring less electrical energy to provide electrons at a low potential for production of H_2 or direct electron feeding [12]. However, sources of sulfide and organic wastes are more limited and microbial catalysts are required for effective recovery of the available electrons [12,15], complicating reactor design.

Candidate microorganisms for production of electrobiocommodities

Methanogens

A very direct E-BC strategy is conversion of carbon dioxide into methane. Methane is an excellent fuel and its low solubility facilitates separation. Methanogenic microorganisms can effectively use H_2 or electrochemically reduced methyl red as an electron donor for methane production [16•,17,18]. It has also been proposed that methanogens can directly accept electrons from electrodes, but in each of these studies there was also significant potential for

electrochemical H_2 production [16•,17,18,19••,20]. Recent evidence has suggested that some methanogens might directly accept electrons from other organisms through biological or mineral electrical contacts [21–23], consistent with the potential for methanogens to make extracellular electrical contacts. Providing electrons with electrodes in anaerobic digesters can increase methane yields, upgrading the quality of gas produced [24]. Difficulties in metabolically engineering methanogens might limit expanding the scope of E-BCs beyond methane for which methanogens might be considered as catalysts.

Acetogenic microorganisms

Acetogenic microorganisms are an attractive catalyst for the conversion of carbon dioxide to a diversity of multicarbon organic products [8••,9••] that might have greater market value than methane. In natural environments acetogens reduce carbon dioxide to acetate with H_2 as the electron donor via the Wood-Ljungdahl pathway, which is the most energetically efficient known pathway for the reduction of carbon dioxide to organic commodities with H_2 as the electron donor [25••]. The Wood-Ljungdahl pathway is also the only autotrophic carbon fixation pathway that can be coupled with energy conservation [26]; it is a form of anaerobic respiration. This is an important consideration when developing self-sustaining systems for E-BC production. Furthermore, energy yield from the Wood-Ljungdahl pathway is low and ca. 95% of the carbon and electron flow during H_2 oxidation coupled to carbon dioxide reduction is diverted to production of small organic endproducts excreted from the cell, rather than production of biomass [25••]. Thus, recovery of energy inputs in desired products is high.

Acetate can be an important commodity and precursor in some chemical syntheses [9••]. Under the appropriate conditions some acetogens will produce high titers of ethanol rather than acetate and in some instances 2,3-butanediol, lactate, butyrate, and butanol are also produced in wild-type cells [9••,27].

Furthermore, genetic manipulation of two acetogens, *Clostridium ljungdahlii* [28–31] and Clostridium sp. MAceT113 [32,33], has been reported and the development of improved genetic tools for *Clostridia* species continues to advance rapidly [25••,34]. Acetyl-CoA, the central intermediate in the Wood-Ljungdahl pathway, is an excellent building block for the production of a diversity of commodities [9••,25••]. Thus, there is the potential for redirecting carbon and electron flow toward the production of more valuable products. For example, genetic engineering of *Clostridium* sp. MAceT113 eliminated genes essential for the production of acetate and ethanol with the introduction of genes for acetone production, yielding a strain that produced high titers of acetone in a syngas reactor [33]. A strain of *C. ljungdahlii* capable of producing small amounts of butanol was created by introducing required genes on a plasmid [28] and strains of *C. ljungdahlii* in which genes were deleted to eliminate the production of acetate and ethanol production have been described [29].

Production of E-BCs with acetogens is not limited to electrochemically generating H_2 or formate as an intermediary electron carrier because a number of acetogens are capable of electrosynthesis; directly accepting electrons from electrode surfaces for carbon dioxide reduction [4••,5]. Biofilms of *Sporomusa ovata* accepted electrons from a graphite cathode reducing carbon dioxide primarily to acetate, with the production of small quantities of 2-oxobutyrate [4••]. Recovery of electrons consumed in these organic products was over 85%, demonstrating the high efficiency expected for biocommodity production via the Wood-Ljungdahl pathway. Evaluation of a diversity of potential cathode materials demonstrated that simply providing positive charge at the cathode surface could increase rates of electrosynthesis sevenfold [35•].

Other acetogens capable of electrosynthesis are: additional *Sporomusa* species, *Morella thermoacetica*, and several *Clostridium* species, including the genetically tractable *C. ljungdahlii* [5]. The abundance of microbes closely related to known *Acetobacterium* species attached to graphite cathode material in a mixed-culture system producing acetate suggested that microorganisms in this genus might also be capable of electrosynthesis [19••]. However, in pure culture *Acetobacterium woodii* was not capable of electrosynthesis [5] and there was the possibility that H_2 was being produced in the mixed culture system [19••].

C. ljungdahlii is an early candidate as a chassis organism for production of E-BCs, either with H_2 or electrosynthesis because it can be genetically manipulated [29]. However, basic features of the physiology of this organism that are important for evaluating what metabolic pathways might be feasible, such as mechanisms for energy conservation [30] and mechanisms for electron transfer from electrodes to cells [31], are only beginning to be explored.

Oxygen-reducing microorganisms

Another approach to E-BC production is to support the growth of aerobic microorganisms with electrochemically produced electron donors such as H_2, formate, or ammonia [13•,14•]. *Ralstonia europea* growing on electrochemically produced formate with oxygen as the electron acceptor was engineered to produce small amounts of isobutanol and 3-methyl-1-butanol [14•]. Ammonia produced electrochemically from nitrite served as the electron donor for growth of *Nitrosomonas europaea*, which oxidized ammonia to nitrite with oxygen as the electron acceptor and used carbon dioxide as its sole carbon source to produce biomass [13•].

However, aerobic microbial physiologies in which the proportions of electrons consumed in oxygen reduction, and carbon diverted to biomass, are high are inherently inefficient for commodity production [36]. This contrasts with the anaerobic systems described above which have evolved physiologies with high flux (>90%) of electrons directly to carbon dioxide reduction with the production of organic compounds that are excreted from the cells. For example, from the information provided [14•], it can be calculated that less than 5% of the electrons consumed during electrochemical production of isobutanol and 3-methyl-1-butanol with *R. europea* were recovered in these products. High biomass production (OD ca. 2) and less than 160 mg/l of products also suggest that most of the carbon dioxide that was fixed was diverted to biomass. In studies with *N. europaea* in which biomass production was the goal, the energetic efficiency was less than 5% [13•]. Additional inefficiencies in aerobic systems include reduction of oxygen at the cathode, which can also produce deleterious reactive oxygen species [14•]. In H_2-based systems the reactivity of H_2 and oxygen is an additional concern [13•].

Conclusions

Producing organic commodities from carbon dioxide with microorganisms powered with electricity is a new concept. There are very few published studies on this topic. Although there are many potential advantages to the E-BC approach, there are many uncertainties related to scalability and commercial competitiveness. Anaerobic processes in which carbon dioxide serves as an electron acceptor are expected to be more efficient than growing microorganisms on electrochemically generated electron donors with oxygen as the electron acceptor. However, it is not yet clear whether directly providing electrons at an electrode surface or generating H_2 or formate as the donor for anaerobic respiration will be the more scalable process. Lower energy inputs are required for direct electron feeding because producing H_2 or formate requires lower cathode potentials, but engineering large reactors with high-density cathode arrays may be an engineering challenge. Basic research into the poorly understood mechanisms for electrode-to-microbe electron exchange (Box 1) would make the engineering of direct electron exchange strategies less empirical.

Box 1 The search for electrotrophs and how they function

The concept of supporting microbial respiration with electrons directly supplied from an electrode is in its infancy in comparison to the decades of research on autotrophic electron donors such as H_2. However, since the discovery in 2004 that *Geobacter* species could directly accept electrons for the reduction of commonly considered electron acceptors such as fumarate and nitrate [37], it has been found that a wide diversity of microorganisms can access cathodes as an electron donor for the reduction of a range of electron acceptors. These include metals and chlorinated solvents, which have applications in bioremediation, and protons for hydrogen production [2,3,38•]. A number of additional pure cultures capable of functioning as electrotrophs have been recently identified [39–43].

There are several potential mechanisms for electron transfer into cells [38•]. Studies to date have focused on the reduction of fumarate and have suggested that electron transfer into *Shewanella oneidensis* employs the same outer-surface contacts as for electron transfer from cells to electrodes [39], whereas electron transfer into and out of *G. sulfurreducens* may proceed via different routes [44]. Strategies for energy conservation have been proposed but not experimentally verified [2,38•]. Microorganisms that do not have a native facility for electronically interacting with electrodes might be turned into electrotrophs with amendments that enhance microbe-electrode interactions [45,46•]. Further investigation of the diversity and function of electrotrophs is likely to expand the options for designing systems for producing commodities with electrical energy as well as additional applications, such as bioremediation.

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