Journal of Industrial Microbiology & Biotechnology (2020) 47:863–876
https://doi.org/10.1007/s10295-020-02309-0

SIMB
Society for Industrial Microbiology and Biotechnology

ENVIRONMENTAL MICROBIOLOGY - MINI REVIEW

Extracellular electron uptake by autotrophic microbes: physiological, ecological, and evolutionary implications

Dinesh Gupta[1] · **Michael S. Guzman**[2] · **Arpita Bose**[1]

Received: 30 June 2020 / Accepted: 7 September 2020 / Published online: 15 September 2020

Abstract
Microbes exchange electrons with their extracellular environment via direct or indirect means. This exchange is bidirectional and supports essential microbial oxidation–reduction processes, such as respiration and photosynthesis. The microbial capacity to use electrons from insoluble electron donors, such as redox-active minerals, poised electrodes, or even other microbial cells is called extracellular electron uptake (EEU). Autotrophs with this capability can thrive in nutrient and soluble electron donor-deficient environments. As primary producers, autotrophic microbes capable of EEU greatly impact microbial ecology and play important roles in matter and energy flow in the biosphere. In this review, we discuss EEU-driven autotrophic metabolisms, their mechanism and physiology, and highlight their ecological, evolutionary, and biotechnological implications.

Keywords Extracellular electron uptake (EEU) · Chemoautotrophy · Photoautotrophy · Photoferrotrophy · Biogeochemical cycle

Introduction

The microbial envelope is an electrically nonconductive, physically impermeable barrier to insoluble materials (e.g., minerals and electrodes) that partitions the interior metabolic activities of cells from the outer environment [2, 131]. Microbial cells have evolved elaborate mechanisms to extract electrons from insoluble electron donors using a process called extracellular electron uptake (EEU). To accomplish this, microbes use both direct and indirect electron transfer pathways, which typically involve electron transfer proteins, such as multiheme *c*-type cytochromes. These proteins enable microbes to oxidize solid electron donors and to drive essential metabolic processes [52, 131]. This process permits microbial survival in environments where soluble electron donors are limiting. Microbial electron exchange with redox-active minerals, or other microbial cells also supports vital ecological processes. Collectively, these processes shape microbial community interactions and influence the geochemistry of the Earth's surface. Microbes can also use poised electrodes mimicking redox active minerals to drive microbial metabolisms with electricity. A summary of the known diversity of EEU-driven autotrophy in nature is depicted in Fig. 1.

EEU mechanisms move electrons from the extracellular space to intracellular electron transport chains. This is generally achieved by direct physical contact (via an outer membrane electron conduit) or indirectly via electron shuttles (redox-active small molecules that can diffuse through the outer cellular envelope). The capability of microorganisms to carry out EEU is typically assessed using bioelectrochemical systems, where an electrode poised at or near the midpoint potential of natural minerals serves as the sole electron donor or acceptor for microbial metabolism [13, 88, 115]. These bioelectrochemical systems are similar to those used to study organisms capable of extracellular electron transfer, such as iron reducers [50, 121], methanogens [27, 146], acetogens [106, 107], sulfate reducers [1, 34, 35], sulfur oxidizers [25], neutrophilic iron oxidizers [68, 140], acidophilic iron oxidizers [68], and anoxygenic phototrophs [13, 22, 54].

Dinesh Gupta and Michael S. Guzman contributed equally to this work.

✉ Arpita Bose
abose@wustl.edu

[1] Department of Biology, Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130, USA

[2] Biosciences and Biotechnology Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA, USA

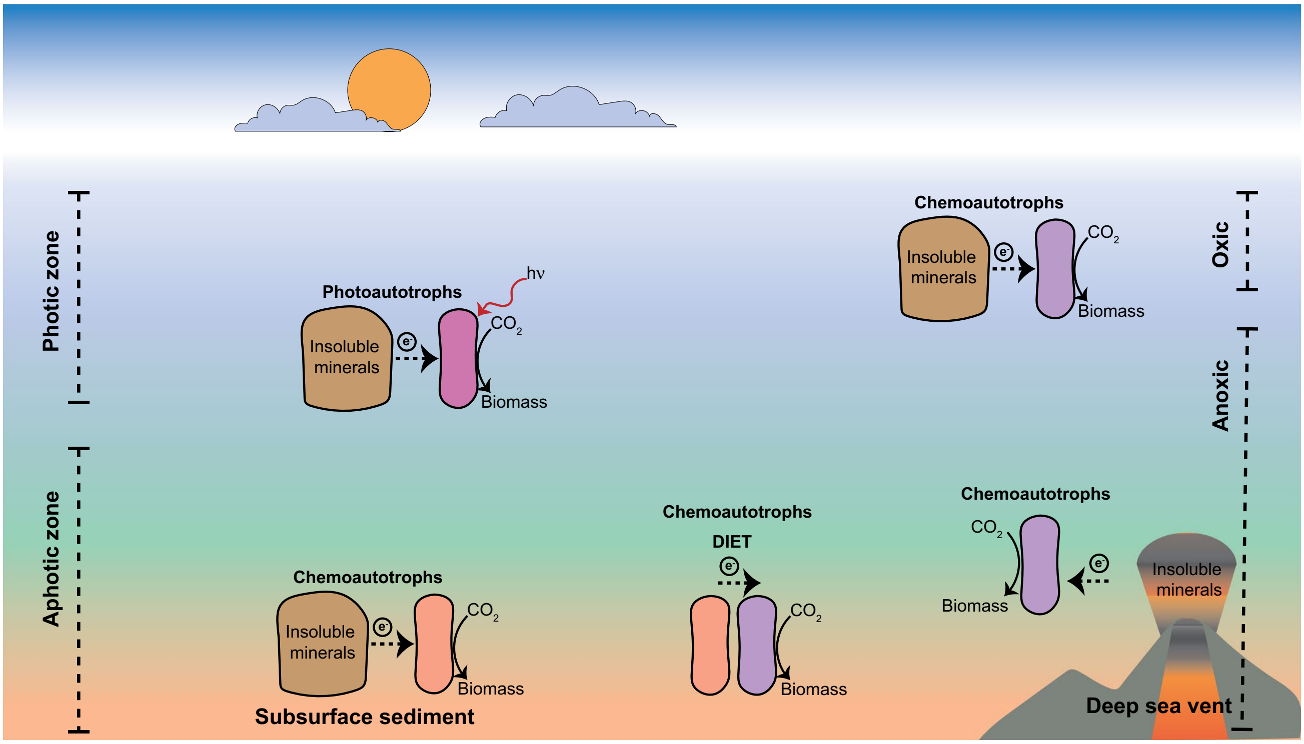

Fig. 1 Diversity of EEU capable autotrophs in natural environment. Extracellular insoluble electron donors (redox-active minerals/cells/natural electrode) support microbial autotrophy in different environmental niches, such as anoxic and aphotic zone likes subsurface sediments and deep-sea vent; anoxic and photic zone; oxic and photic or aphotic zone

EEU is a physiologically diverse process that is present in multiple bacterial lineages. However, the molecular and bioenergetic underpinnings of this process remain poorly understood. This is especially true for autotrophic bacteria, which catalyze the conversion of carbon dioxide (CO_2) into biomass using electron transport chains powered by light (photoautotroph) and/or chemical (chemoautotroph) energy [53, 68]. Thus, these organisms may play a fundamental role in carbon cycling in terrestrial and aquatic ecosystems.

Improving our understanding of EEU mechanisms is critical from both an evolutionary and a biotechnological standpoint [53, 75, 132]. The availability on an early Earth of insoluble inorganic electron donors from volcanic and hydrothermal sources could have supported autotrophic EEU metabolisms on a global scale [20]. Consistent with this, recent studies link autotrophic pathways of extant microbes to extracellular electron uptake [52]. In addition, there is substantial interest in exploiting EEU for microbial electrochemical technologies, including microbial electrosynthesis, bioelectronics, and bioremediation [27, 90, 115, 116]. Owing to the ecological relevance and prevalence of EEU capable autotrophs in nature, and their emerging biotechnological interest, here we will focus on the utilization of EEU by autotrophs to derive CO_2 assimilation into chemicals. We discuss the ecological and evolutionary implications of EEU, its molecular underpinnings and physiology, as well as the biotechnological applications.

Ecological and evolutionary implications of extracellular electron uptake

Autotrophs are important primary producers that drive fundamental ecological processes, either using light energy (photoautotrophs) or using energy derived from chemosynthetic reactions (chemoautotrophs). Emerging evidence suggests that, unlike eukaryotes, autotrophic microbes can extract electrons from insoluble materials (e.g., minerals and electrodes or other cells) for energy generation and CO_2 fixation. Insoluble electron donors are abundant in nature and may enable autotrophic microbes to thrive in niches with a scarcity of soluble electron donors. Indeed, bioelectrochemical studies using carbon/graphite electrodes show that a wide range of geochemically relevant redox potentials can support EEU-driven metabolisms [53, 68, 82, 123]. Furthermore, electroactive microbes often utilize conserved mechanisms to take up electrons from electrodes and from natural insoluble electron donors [52, 53, 68]. These findings provide new insights into the diversity of insoluble electron donors that could support microbial primary productivity.

Understanding microbe–mineral interactions at the community level is an important challenge in geomicrobiology. Bioelectrochemical systems have been applied to understand microbial community interactions among autotrophs, namely ANME-SRB [100, 126, 135, 150] and syntrophic anoxygenic phototrophs [54], as well as in situ lithoautotrophic microbial communities [123]. Furthermore, studies of electrochemical microbial communities have revealed a diversity of metabolic interactions, such as direct interspecies electron transfer (DIET) and long-range extracellular electron transfer [88]. These electron-transfer reactions may greatly impact microbial energy flow and biogeochemical carbon cycling on Earth. Understanding these interactions at the molecular level is also of upmost importance for engineering applications, such as bioremediation and microbial electrosynthesis.

Two groups of microbial autotrophs hypothesized to have ancient origins include anoxygenic photoferrotrophs and anaerobic chemolithotrophs. Photoferrotrophy represents a modern analog of a microbial metabolism that may have prevailed on early Earth's soluble iron-rich and oxygen-limited conditions [20]. Photoferrotrophy is thought to be one of the most ancient forms of photosynthesis [153] and evidence suggests it could be responsible for the deposition of the Archean banded iron formations (BIFs) [39, 73, 79, 112, 152]. Recently, it has been shown that EEU processes are the cornerstone for photoferrotrophy [52]. In addition, chemolithotrophs, such as acetogens and methanogens, assimilate CO_2 via the Wood–Ljungdahl pathway and can survive under metabolically stringent conditions [9, 94]. The Wood–Ljungdahl pathway is energetically economical, and it is considered amongst the most primitive carbon fixation pathways [84]. Studies have shown that chemoautotrophs that encode the Wood–Ljungdahl pathway have the capability to drive CO_2 fixation using insoluble electron donors via extracellular electron uptake [27, 38, 106, 107]. Together, this could point to an ancient origin for EEU-driven carbon assimilation for both photoautotrophs and chemoautotrophs. It is thought that the reducing conditions of early Earth may have favored the incorporation of soluble and freely available Fe(II) into biomolecules [28], thereby making Fe(II) an essential component of biological systems. Accordingly, the ubiquity of iron-containing electron transfer proteins, such as multiheme cytochrome *c* and iron–sulfur proteins, in EEU processes [10, 71, 129, 130] further support the idea that these EEU-driven autotrophic metabolisms may have evolved on early Earth and may have been crucial in shaping these ecosystems.

Microbe–mineral interactions play an important role in biogeochemical processes on Earth. Microbes that can utilize insoluble electron donors for cellular metabolism via extracellular electron uptake are important for nutrient cycling in soils, aquatic sediments, and subsurface environments. Physiological studies of autotrophic microbes have recently shown that EEU-driven carbon assimilation may be an important ecological sink for inorganic carbon. Ecological, genetic, and biogeochemical studies of microbes capable of EEU, however, have lagged in comparison to studies of the microbes capable of extracellular electron transfer to insoluble electron acceptors. Emerging electrochemical and systems biology approaches are enabling microbiologists to probe the contribution of EEU-driven microbial processes at both the single cell and ecosystem scale.

Our current understanding of EEU processes is limited to a few naturally occurring electron donors. Recently, it has been shown that other materials, such as carbon/graphite electrodes poised at naturally relevant mid-point potentials could serve as electron donors for autotrophic microbes. EEU is also important for the evolution of key ecological interactions between microbes. Besides the ecological and evolutionary importance, EEU processes are also important for the biotechnological applications. Currently, these applications are limited due to the recalcitrant nature of these microbes, inadequate knowledge of EEU mechanisms, and lack of genetic engineering tools [113]. Future studies focusing on determining the molecular underpinnings of EEU, and developing engineering toolkits, will help advance this emerging biotechnological endeavor and improve our understanding of the broader environmental implications of these processes.

Extracellular electron uptake-driven autotrophic metabolisms and their mechanisms

Iron-oxidizing chemoautotrophs

Much of what we know about EEU comes from studies of microorganisms that oxidize iron minerals, such as ferrous sulfide (FeS), siderite ($FeCO_3$), pyrite (FeS_2), magnetite (Fe_3O_4), and green rust [18, 56, 72, 73]. Fe(II)-oxidizing chemoautotrophs use iron minerals as electron donors for growth [10, 80]. For example, in acidic environments, such as acid mine drainage ecosystems oxygen is typically the only bioenergetically favorable terminal electron acceptor for microbial iron oxidation [10, 65]. The redox potential of the O_2/H_2O couple is + 1200 mV vs SHE at pH 2, which is more electropositive than at neutral pH (+ 820 mV vs SHE). This favors the use of Fe(II) oxidation (Fe(II)/Fe(III), + 770 mV) by chemolithoautotrophic acidophiles. In addition, even though the energy gain is low and Fe(II) is prone to spontaneous abiotic oxidation by oxygen at circumneutral pH, neutrophilic iron-oxidizing bacteria have also evolved the capability to thrive in iron-rich microaerophilic environments.

Together both acidophilic and neutrophilic chemolithoautotrophs have evolved to grow by linking Fe(II) oxidation to oxygen (O_2) reduction at the microoxic interface using specialized electron transport chains [60]. This process generates sufficient cellular energy (ATP) and reducing equivalents (NAD(H)) for carbon assimilation and biosynthesis [53, 68]. Bacteria capable of chemoautotrophic Fe(II) oxidation include acidophilic bacteria, such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* [45, 103]; neutrophilic marine bacteria *Gallionella ferruginea*, *Mariprofundus ferrooxydans* PV-1; and neutrophilic freshwater bacteria, such as *Gallionella capsiferriformans* ES-2 and *Sideroxydans lithotrophicus* ES-1 [41, 42, 55].

Genetic studies of Fe(II)-oxidizing chemoautotrophs have revealed two divergent cytochrome *c*-based extracellular uptake pathways: a Cyc2-based pathway and a MtoAB/PioAB mediated pathway (Fig. 2). Gene clusters encoding these pathways have been identified in the genomes and metagenome-assembled genomes (MAGs) from diverse bacterial genera [47, 97, 98]. Phylogenomic investigations of both the Cyc2 and MtoAB/PioAB pathways have revealed their broad distribution among chemoautotrophic Fe(II)-oxidizing bacteria, including freshwater *Gallionellaceae* spp. and marine Zetaproteobacteria [58].

The Cyc2-based pathway (Cyc2/Rus/Cyc1) was first identified in *A. ferrooxidans* [4, 68]. In this bacterium, electrons from Fe(II) are transported along its electron transport chain to reduce O_2 [4]. The process was first proposed by Ingledew [65] and its molecular [3, 155], genomic [114, 144], and biochemical [23, 156] aspects are well studied. The Fe(II) oxidation module in acidophilic chemoautotrophs (Fig. 2a) is composed of an outer membrane monoheme *c*-type cytochrome-porin fusion protein (Cyc2) [24], the periplasmic blue copper protein rusticyanin (Rus), an inner membrane-bound cytochrome *c*4 (Cyc1), and an *aa*3-type cytochrome oxidase (CoxBACD) in the inner membrane where O_2 is reduced (reviewed in [10]). Cyc2 has been proposed to oxidize Fe(II) extracellularly and transfer electrons to the periplasmic rusticyanin, where it feeds electrons to either a down-hill (exergonic) pathway to generate a proton gradient from the reduction of O_2, and also to an uphill (endergonic) pathway to generate NAD(H) [26] through reverse electron flow (reviewed in [10]). Rusticyanin represents a "branch point" that balances ATP and NAD(H) generation (Fig. 2a), which are both required for carbon fixation via the Calvin–Benson–Bassham (CBB) cycle [44, 68]. The role of the Cyc2/Rus/Cyc1 system in electron uptake from electrodes has been investigated using site-specific chemical marking experiments [68]. Inhibition of cytochrome *c* oxidases with carbon monoxide leads to a disruption in electron uptake suggesting the down-hill pathway is active during EEU. Also, inhibition of cytochrome bc_1 with chemical probes leads to a decrease in current uptake. However, this decrease is observed to be subtle and transient therefore it is unclear how active the "up-hill"/reverse electron flow pathway is under these conditions. Detailed genetic studies are required to resolve the role of the Cyc2/Rus/Cyc1 system in this process. Lastly, comparative genetic and genomic studies suggest that the physiology of EEU is conserved among chemoautotrophic iron-oxidizing bacteria. Like acidophilic, neutrophilic iron-oxidizing chemoautotrophs, such as *S. lithotrophicus* ES-1 and *M. ferrooxydans* PV-1 use CBB cycle for CO_2 fixation [5, 40].

Cyc2 homologs have also been characterized in the acidophilic Fe-oxidizing bacterium *Leptospirillum* sp. (Cyc_{572}) [70] and in the marine neutrophilic iron-oxidizing bacterium, *M. ferrooxydans* PV-1 ($Cyc2_{PV\text{-}1}$) [5]. Proteomic profiling of *M. ferrooxydans* PV-1 was used to predict the iron-oxidation pathway in this neutrophilic chemoautotroph (Fig. 2b), where Fe(II) is oxidized by the outer membrane $Cyc2_{PV\text{-}1}$. Electrons are then transferred to the periplasmic cytochrome *c*4 ($Cyc1_{PV\text{-}1}$), and finally, to O_2 via the intracytoplasmic membrane *cbb3*-type cytochrome oxidase [5]. Cyc2 homologs have also been identified in the genomes of several neutrophilic Fe-oxidizing isolates in the *Zetaproteobacteria* and *Gallionellaceae* genera [58, 75, 97]. Furthermore, environmental studies have shown that Cyc2 homologs are prevalent in hydrothermal vent microbial communities, suggesting that the Cyc2 iron oxidation pathway might be relevant in iron cycling in these ecosystems [98]. However, genetic and biochemical studies are needed to confirm the gene-to-function relationship. For example, the biophysical details of how electrons are transported across the outer membrane via the monoheme cytochrome *c*-porin Cyc2, awaits elucidation.

The porin–cytochrome system MtoAB has been implicated in extracellular iron oxidation in the neutrophilic iron-oxidizing chemoautotroph, *S. lithotrophicus* ES-1 [85]. This system (Fig. 2c) comprises MtoA (a decaheme cytochrome *c*), MtoB (an outer membrane porin), MtoD (a soluble periplasmic monoheme cytochrome *c*) and CymA (an inner membrane tetraheme *c*-type cytochrome) [7, 40, 85]. The MtoA and MtoB proteins are homologs of PioA/MtrA and PioB/MtrB proteins, respectively. This suggests that MtoAB transfers electrons across the outer membrane from the extracellular insoluble iron minerals (Fig. 2c) [7, 85, 130]. The electrons are then likely shuttled by MtoD to CymA, a quinone oxidoreductase in the inner membrane, where electrons can be transferred to the quinone/quinol pool [7, 85]. This porin–cytochrome system is present in several other chemoautotrophic iron-oxidizing bacteria with some variation of the periplasmic cytochrome *c* electron shuttle (Fig. 2d) [58, 59]. Under anaerobic condition, these chemoautotrophs can divert the electrons to nitrate using a membrane-bound, cytoplasmic nitrate reductase to reduce nitrate to ammonium (Fig. 2d) [59]. Unlike Cyc2,

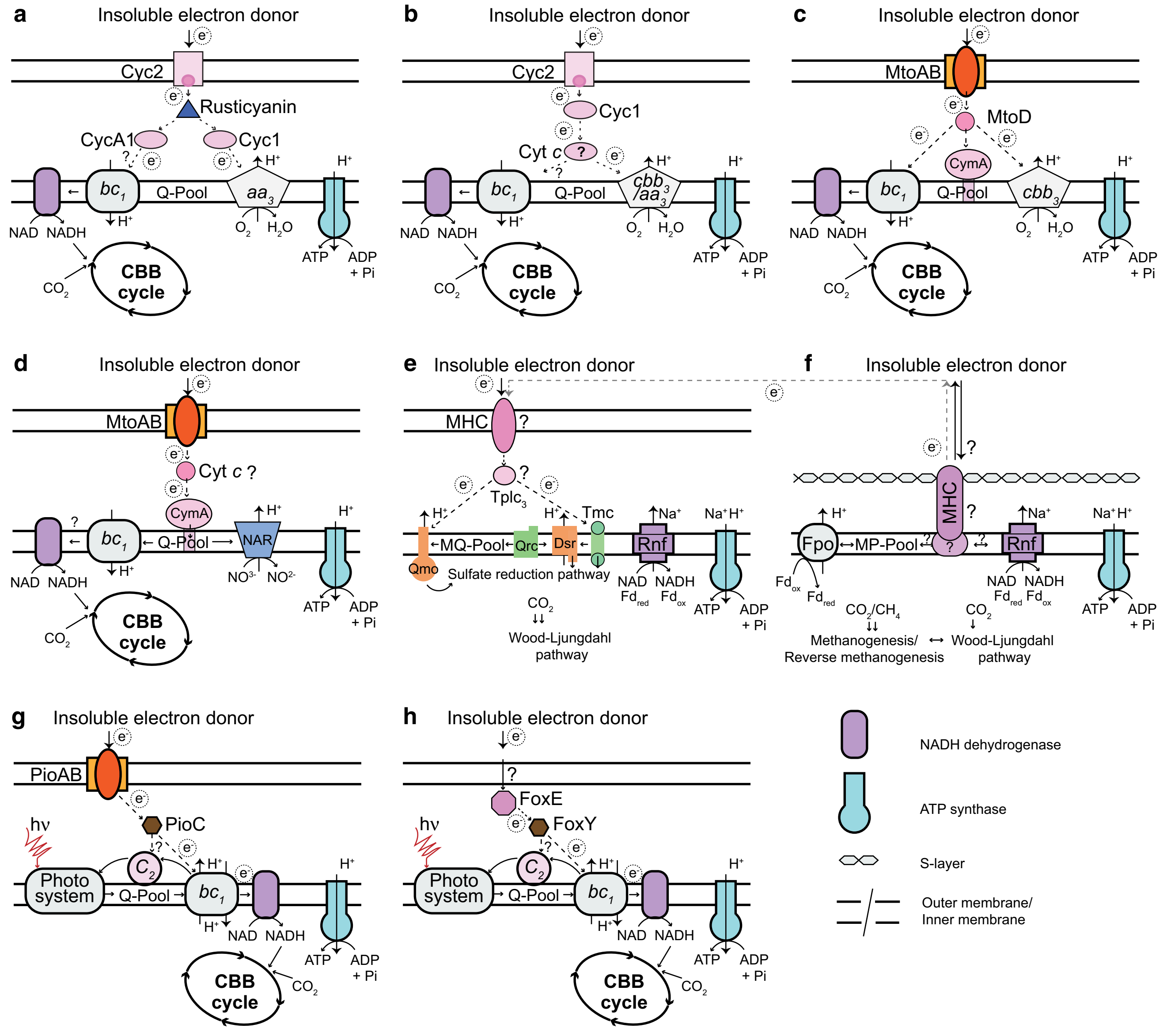

Fig. 2 Models of extracellular electron uptake (EEU)-driven microbial autotrophy. Cyc2-based models of EEU for acidophilic (**a**) and neutrophilic chemoautotrophs (**b**); MtoAB-based models of EEU for microaerophilic (**c**) and anaerobic chemoautotrophs (**d**); MHC-based models of EEU for sulfate reducing (**e**) and methanogenic (**f**) chemoautotrophs; PioAB-based model of EEU (**g**) and FoxEYZ-based model of EEU (**h**) in anoxygenic photoautotrophs. Autotrophs access extracellular insoluble electron donors (redox-active minerals/cells/electrode) via outer membrane electron transfer protein or proteins complex; the electron is then shuttle to inner membrane respiratory/photosynthetic electron transport system by periplasmic electron-shuttle proteins; the electron is then finally used to reduce O_2 (aerobic/microaerobic chemoautotrophs) or NO^{3-} (anaerobic chemoautotrophs) or NAD^+ (anoxygenic photoautotrophs). These processes generate proton motive force which is used to produce ATP via ATP synthetase. The proton motive force is also used to produce NADH by reverse electron flow and generated NADH is used to fix CO_2 via CBB cycle. Microbes are also known to use EEU to fix CO_2 via Wood–Ljungdahl pathway. *Q* ubiquinone, *MQ* menaquinone, *MP* methanophenazine, *bc*$_1$ *bc*$_1$ complex, *aa3/cbb3* *aa3*-type/*cbb3*-type cytochrome oxidase, *Tplc*$_3$ periplasmic tetraheme type 1 cytochrome c$_3$, *Qrc/Tmc* inner membrane redox complexes, *QmoABC (Qmo) and DsrMKJOP (Dsr)*, membrane-associated quinone-interacting oxidoreductase complexes, *Rnf* Rnf complex (energy-converting ferredoxin: NAD^+ reductase complex)

MtoAB-containing chemoautotrophs have not been tested for their ability to perform EEU from electrodes.

Sulfate-reducing chemoautotrophs

Sulfate-reducing bacteria (SRB) couple the anaerobic oxidation of sulfate to the oxidation of organic compounds. Chemoautotrophic growth by SRB can also be accomplished using H_2 as an electron donor for carbon fixation via the reductive tricarboxylic acid (TCA) cycle or the reductive acetyl-CoA pathway (Wood–Ljungdahl pathway) [69, 125]. The earliest discovery of EEU by SRB came from studies of microbially-induced iron corrosion [37]. These studies use elemental iron granules as the sole electron donor to enrich SRB. Bioelectrochemical investigations demonstrated the ability of several SRB to take up electron from electrodes with CO_2 as the sole source of carbon. These EEU SRB include *Desulfosporosinus orientis* and *Desulfovibrio piger* ($E_{applied}$: − 310 mV vs. SHE) [33], *Desulfopila corrodens* strain IS4 ($E_{applied}$: − 400 mV vs. SHE) [8], *Desulfobacterium autotrophicum* HRM2 ($E_{applied}$: − 500 mV vs. SHE) [159]. In the lithotrophic marine SRB *Desulfovibrio ferrophilus* IS5, an outer membrane cytochrome could provide an electron conduit for EEU from electrodes ($E_{applied}$: − 400 mV vs. SHE) for sulfate reduction [34]. Several outer membrane multiheme cytochromes in *D. ferrophilus* IS5 are overexpressed under nutrient limitation. Furthermore, transmission electron microscopy of starved *D. ferrophilus* IS5 cells revealed heme-containing extracellular appendages reminiscent of the protein nanowires of iron reducers [120]), suggesting it may utilize direct uptake mechanisms [34].

SRB have been identified that form syntrophic consortia with anaerobic methanotrophic (ANME) archaea. These microbial consortia catalyze sulfate reduction, coupled to anaerobic methane oxidation, and are thought to be an important methane sink in marine sediments [78, 119]. In this association, ANME oxidize methane (CH_4) to CO_2 via reverse methanogenesis, and transfer the electrons to SRB via direct interspecies electron transfer (DIET) for sulfate reduction [100, 126, 135, 150]. The molecular mechanism of the cooperative electron exchange in the ANME-SRB consortia has been hypothesized to follow DIET, [100, 150] a process previously reported for methanogenic consortia [122, 139]. Electron exchange may involve outer membrane multiheme cytochrome *c* proteins of encoded by the syntrophic partners [100, 126, 150]. Both ANME and SRB have outer membrane multiheme cytochrome *c* proteins that could participate in the electron transfer [100, 135]. This hypothesis is further supported by metatranscriptomic [102, 148] and in situ metaproteomic [135] studies from marine methane seep sediments. Comparative genomic evidence suggests that the outer membrane multiheme cytochrome *c* of these syntrophic microbes are similar in organization to cytochromes mediating extracellular electron transfer in metal-reducing bacteria, such as *Geobacter* and *Shewanella* [77, 100, 135].

The mechanistic underpinnings of EEU are poorly understood in SRB. Both direct and indirect mechanisms have been proposed. Indirect mechanisms, such as abiotic H_2 evolution, could be prevalent because a majority of SRB possess periplasmic hydrogenases [1]. Certain SRB, however, have been shown to generate cathodic current under electrochemical conditions more positive than the thermodynamic potential for cathodic H_2 production, suggesting direct electron uptake mechanisms could exist [8, 33, 34]. In addition, the SEEP-SRB1 clade of ANME partners lack periplasmic hydrogenases [135] and are incapable of growth with H_2 as an electron donor [105, 151]. One model (Fig. 2e) (either for free living or syntrophic SRB) proposes the involvement of an outer membrane multiheme cytochrome *c* for direct EEU from insoluble electron donors (elemental iron or electrode, or ANME partner in consortia) [1, 34, 135]. The electrons are then thought to be shuttled by a conserved periplasmic tetraheme type 1 cytochrome c_3 ($Tplc_3$) to the inner membrane complexes Qrc or Tmc. The Qrc complex reduces the menaquinone pool, which then transfers the electrons to the inner membrane quinone-interacting oxidoreductase complexes, QmoABC (Qmo) and DsrMKJOP (Dsr). These complexes are hypothesized to transfer electrons to cytoplasmic sulfate reduction pathway, which contributes to the transmembrane proton gradient. The Tmc complex can also transfer electrons from $Tplc_3$ to menaquinone pool or to a cytoplasmic sulfate reduction pathway (for details of this proposed model refer to refs [1, 135]).

Acetogens

Acetogens are strictly anaerobic bacteria that grow by the conversion of C1 compounds (e.g. formate, CO, or CO_2) to acetate via the acetyl-CoA pathway (Wood–Ljungdahl pathway) [38]. Acetogens can also use molecular hydrogen (H_2), electrodes [106, 107] or metallic iron (Fe^0) [76, 111] as electron donors to reduce CO_2. A variety of acetogens have been isolated using electrodes and metallic iron as electron donors [76, 92, 111]. Several acetogenic microbes, including *Sporomusa* and *Clostridium* species, produce organic compounds from CO_2 using electrodes [106]. Their high carbon conversion efficiency shows promise for microbial electrosynthesis applications [90, 116]. This very same efficiency also makes Fe^0-oxidizing acetogens major drivers of iron biocorrosion [43].

Studies suggest that acetogens use both direct and indirect mechanisms for extracellular electron transfer. Outer membrane cytochromes have been proposed to provide a direct pathway for electron transport in *Sporomusa spp*.[75, 76, 106, 107, 122]. Acetogens can also reportedly take up electrons from cathodes [106] or Fe^0 [76, 111] under conditions unfavorable for electrochemical H_2 production. However, the underlying molecular mechanisms are not known. Acetogens may also use indirect extracellular electron transfer mechanisms via soluble electron shuttles and H_2 generation [64]. Many microbes are known to secrete redox-active small molecules, such as flavins and phenazines, to shuttle electrons to extracellular electron acceptors [14, 48, 81, 93, 149]. Supplementation of bioelectrochemical systems with artificial mediators stimulates EEU rates by certain acetogens [136]. However, the natural production of soluble electron shuttles by acetogens is not known [111] and thus, its environmental relevance is unclear. Indirect electron uptake by acetogens through H_2 production at the solid interface has been experimentally corroborated. An anoxic corrosion reaction at the surface of Fe^0 generates H_2, for acetogenesis [110]. Recent studies also show that cell-free spent media from electroactive acetogens can increase H_2 production at electrodes compared to abiotic conditions. For example, cell-free spent media of *Sporomusa sphaeroides* [36] and *Sporomusa ovata* [141] can enhance H_2 generation at cathodes poised at − 500 mV and − 300 mV vs. SHE, respectively. These studies suggest that microbial cells secrete enzymes, such as hydrogenases, that can absorb onto the solid surface to generate H_2. Although methanogens are known to excrete hydrogenases for Fe^0-driven H_2 generation [143], such enzymes have not been detected in the spent medium of acetogens [110].

Methanogens

Methanogenesis is a widespread biogeochemical process on Earth that primarily occurs in anoxic, organic-rich terrestrial, and marine subsurface environments [6, 96]. Methane is typically produced in heterotrophic microbial communities of methanogens and syntrophic bacteria that collectively convert organic acid into methane as an end-product of cellular respiration. Hydrogenotrophic methanogens produce methane by utilizing the end-products of syntrophic bacteria (i.e. H_2) as electron donors to reduce CO_2. The interspecies transfer of electron equivalents, such as H_2 and formate, is generally achieved by a close physical association between syntrophic consortia and methanogens [32, 66, 67].

DIET is also thought to be an important driver of energy and electron transfer in methanogenic microbial communities [89, 99]. This mechanism has been studied in bioelectrochemical systems where electrons produced by electrogenic microbes during the oxidation of organic acids at the anode drive methane production from CO_2 at the cathode [87, 116]. Methanogenic electron uptake from cathodes has been proposed to occur via direct extracellular electron transfer process [27]. Methanogens, such as *Methanosarcina barkeri* can utilize electrons directly from syntrophic bacteria, such as *Geobacter metallireducens* via DIET, or electrodes [158].

Whether from syntrophic bacteria or from electrodes, methanogens use a multiheme cytochrome *c* (MHC) for bidirectional electron exchange [62, 122, 133, 139]. The electron transfer pathways that use MHC for methane oxidation or CO_2 reduction have been described in several methanogens [61, 62]. The model is similar to the one proposed for methanotrophic ANME partner in ANME-SRB consortia [100]. In this model (Fig. 2f), reducing equivalents generated during the oxidation of methane reduce the membrane-bound methanophenazine pool via reactions at Fpo and Rnf complexes that generate a proton and sodium ion gradient, respectively. The reduced methanophenazine pool is then oxidized by an integral membrane protein (cytochrome *b*/cytochrome *c*). Electrons can then be transferred to larger MHCs for extracellular electron transfer across the S-layer [100]. The electron transfer in the reverse direction could lead to CO_2 reduction to methane [61].

It is also plausible that methanogens use a cytochrome *c*-independent mechanism that is based on the production of extracellular hydrogenase enzymes [36, 124]. A recent study of multiheme cytochrome *c* in DIET by methanogens demonstrated that (i) multiheme cytochromes *c* are not required for EEU in *M. mazei*, and (ii) these proteins are not widely conserved [157]. In the DIET-dependent methanogen, *M. mazei*, deletion of the predicted MHC encoding gene (MM_0633), has no effect on EEU either from its syntrophic partner, *G. metallireducens*, or from electrodes [157].

Chemoautotrophic microbes, such as acetogens, methanogens, and SRB are known to use a reductive acetyl-CoA pathway or Wood–Ljungdahl pathway to derive their cellular energy and carbon [16, 38, 117]. Because this pathway is thermodynamically limiting, early studies focused on understanding how these organisms derive sufficient energy for growth under such stringent metabolic conditions. The mechanism was ultimately uncovered with the discovery of energy conserving membrane-complex enzymes and the understanding of flavin-based electron bifurcation mechanisms in these microbes (reviewed in [17, 109, 128]). Using electron bifurcation, these microbes split a two-electron-transfer from an electron donor (such as H_2) into two (low and high) potentially different electrons. This allows these microbes to carry out both endergonic and exergonic reactions using the low- and high-potential electrons, respectively, as one-electron transfers without investing cellular energy. The low-potential electron is generally used to reduce ferredoxin. This reduced ferredoxin can be utilized by the energy conserving respiratory enzymes Rnf (energy-converting ferredoxin: NAD^+ reductase complex) and Ech (energy-converting ferredoxin-dependent hydrogenase complex) to reduce NAD^+ and protons, respectively. These processes also generate a transmembrane ion gradient which is utilized for ATP generation (reviewed in [84]). Whether EEU processes are linked to energy conservation via these mechanisms requires further investigation.

Iron-oxidizing phototrophs

Unlike oxygenic phototrophs (e.g., cyanobacteria, algae, and plants), which solely depend upon water splitting for photosynthesis, anoxygenic phototrophs use both soluble and insoluble electron donors. This includes Fe(II) and insoluble mixed-valence iron minerals, using a process called photoferrotrophy [152]. Photoferrotrophy was first reported in purple bacteria [152]. This process has since been described in purple sulfur, purple nonsulfur, and green sulfur bacteria (reviewed in [19]). Several anoxygenic phototrophs studied in bioelectrochemical systems include the purple nonsulfur bacteria *Rhodopseudomonas palustris* TIE-1, *Rhodomicrobium vannielii,* and *Rhodomicrobium udaipurense* [13, 52] and the green sulfur bacterium *Prosthecochloris aestuarii* [54, 63].

Anoxygenic phototrophs have evolved divergent mechanisms to facilitate microbe electrode and microbe–mineral interactions. One of the best studied systems is PioAB, which is encoded in the genomes of several phototrophs (*R. palustris* TIE-1, *R. vannielii,* and *R. udaipurense*). A putative outer membrane cytochrome homologous to Cyc2 has also been identified in the draft genomes of iron-oxidizing phototrophs, *Chlorobium phaeoferrooxidans* and *Chlorobium* sp. Strain N1 [15, 30]. However, only the PioAB system of *R. palustris* TIE-1 is known to facilitate EEU from solid substrates (e.g., minerals or electrodes) and to link the process to photosynthesis [13, 52, 53]. Therefore, much of the discussion in this section will focus on the molecular details of EEU by *R. palustris* TIE-1, followed by a comparison to the iron-oxidation systems of *Rhodobacter* sp. strain SW2 and related phototrophic bacteria.

Rhodopseudomonas palustris TIE-1 oxidizes soluble Fe(II), insoluble mixed-valence iron minerals, and electrodes using light energy [13, 18, 53, 71]. These processes are catalyzed by proteins encoded in a three-gene operon (PioABC). PioA is a periplasmic decaheme cytochrome *c* protein, PioB, an outer membrane beta-barrel porin, and PioC, a periplasmic high potential iron–sulfur protein (HiPIP) [13, 71]. The molecular mechanisms of phototrophic Fe(II) and electrode EEU have been studied at the molecular and biochemical level (Fig. 2g) [52]. PioA forms a complex with PioB (PioAB) in the outer membrane after periplasmic secretion and processing [52]. The PioAB complex serves as an extracellular electron conduit that transfers electrons from Fe(II) or poised electrodes across the outer membrane [52]. PioA in the complex spans across the outer membrane through PioB and transfers electrons to periplasmic PioC, which then likely transfers electrons to the photosynthetic reaction center in the inner membrane (Fig. 2g) [10, 11, 52, 129]. The PioAB system is conserved in *R. vannielii* and *R. udaipurense*, phototrophs that can also perform EEU from Fe(II)/electrodes [52].

PioA and PioB are homologs of the MtrA and MtrB proteins, respectively of the MtrCAB system of the iron-reducing bacterium *Shewanella oneidensis* MR-1. Although both the PioAB and MtrCAB systems bridge electrons between microbes and the extracellular environment, there are fundamental biophysical and biochemical differences in the electron transfer process. Firstly, extracellular electron transfer, preferably or naturally, occurs in opposite directions. Secondly, the PioAB system has a single decaheme cytochrome *c* (PioA), unlike two decaheme cytochrome *c* proteins (MtrA and MtrC) encoded in *S. oneidensis* MR-1. In addition, PioA homologs in phototrophic bacteria contain a larger N-terminal region compared to MtrA homologs. This N-terminal extension controls heme maturation and its proteolytic cleavage is required to produce decaheme-attached PioA. The post-secretory proteolysis of the extended N-terminal of PioA homologs in these phototrophic bacteria is hypothesized to control the synthesis of bioenergetically expensive decaheme cytochrome *c* [52].

Some phototrophic iron-oxidizing bacteria lack homologs of the PioAB/MtrAB or Cyc2 system. *Rhodobacter* sp. strain SW2 contains a three-gene operon *foxEYZ* encoding FoxE, a periplasmic diheme cytochrome *c*; FoxY, a predicted quinoprotein; and FoxZ, a predicted inner membrane transport protein (Fig. 2h) [29]. Structural studies of FoxE suggest a controlled rate of electron transfer that could allow the periplasmic oxidation of Fe(II) without the formation of lethal Fe(III) precipitates [108]. However, many questions regarding the molecular and physiological nature of this model remain unknown. Currently, it is unclear whether iron-oxidation by *Rhodobacter* sp. strain SW2 involve an EEU mechanism or whether it can oxidize mixed-valence iron minerals or electrodes. Further investigation of the iron oxidation pathway could help determine the precise electron transfer mechanism, and help resolve the location of Fe(II) oxidation.

Some isolates of iron-oxidizing phototrophs lack homologs of known iron oxidation pathways and/or do not have genetic systems. Thus, molecular understanding of iron oxidation in these microbes is lacking. These microbes include *Rhodovulum iodosum* and *Rhodovulum robiginosum*, green sulfur bacteria from the genus *Chlorobium*, and purple sulfur bacteria, such as strain L7 in the genus *Chromatium* [39]. Comparative genome analyses of several phototrophic iron oxidizers have provided some insights into their iron oxidation pathways. The draft genome of *R. robiginosum* DSM12329 does not have clear homologs of proteins known to participate in extracellular electron transfer or iron oxidation pathways but contains several uncharacterized multiheme cytochromes that could play analogous roles [51]. Biochemical, structural, and functional genomic studies could help elucidate whether these genes contribute to electron uptake processes.

Unlike chemoautotrophs, anoxygenic phototrophs utilize cyclic photosynthesis to generate cellular energy and reducing equivalents. The photosystem (photosystem II, P_{870}) of anoxygenic phototrophs is excited by light energy and electrons flow cyclically from the reaction center to the ubiquinone pool to re-oxidize cytochrome *bc*$_1$. This process generates a proton motive force to drive ATP synthesis via cyclic photophosphorylation. Electrons are typically shuttled to the photosystem by periplasmic cytochrome *c*-type proteins. Within the *Rhodospirillaceae*, cytochrome *c*$_2$ and/or high-potential iron–sulfur proteins (HiPIPs) mediate photosynthetic electron transfer between cytochrome *bc*$_1$ and the reaction-center bacteriochlorophyll [145]. External electron donors are required to generate reducing equivalents, namely NAD(H), for biosynthesis. This process is driven by reverse electron transfer mechanisms that push electrons uphill against their electrochemical gradient. This is likely mediated by cytochrome *bc*$_1$ and NADH dehydrogenase which transfer electrons from the ubiquinone pool to reduce NAD^+ to NAD(H). Similar to iron- and sulfur-oxidizing chemoautotrophs, photoautotrophs use CBB cycle for CO_2 assimilation.

Recent studies have suggested that the EEU pathways of anoxygenic phototrophs are linked to energy transduction and carbon fixation via photosynthetic electron transfer [52, 53]. Physiological studies of the electron uptake pathway of *R. palustris* TIE-1 have revealed that EEU from electrodes is catalyzed by a cytochrome *bc*$_1$-mediated process and is dependent upon a functional proton motive force. This could suggest that reverse electron flow is active in *R. palustris* TIE-1 to transfer electrons from poised electrodes, where the redox potential is sufficiently lower than the NAD^+/NAD(H) redox couple. Reverse electron flow has been suggested for phototrophic Fe(II)-oxidizing bacteria and this process is well-studied in chemoautotrophic Fe(II)-oxidizing bacteria. Interestingly, treatment of *R. palustris* TIE-1 biofilms with NADH dehydrogenase-specific inhibitors was shown to cause a substantial defect in electron uptake from electrodes further implicating reverse electron flow processes in reductant generation in this organism [53] (Fig. 2g).

Syntrophic anoxygenic phototrophs

The green sulfur bacterium *Prosthecochloris aestuarii* is also known to utilize EEU to carry out anoxygenic photosynthesis [54]. This bacterium can take up electrons from either solid electrodes or from a syntrophic partner [54]. In the latter case, electrons from acetate oxidation by *Geobacter sulfurreducens* are transferred to *Prosthecochloris aestuarii* via DIET [54]. This mechanism of electron transfer is supported by two-chamber bioelectrochemical studies. In syntrophic association, electrons generated from acetate oxidation by *G. sulfurreducens* in the dark anode chamber drive light and CO_2-dependent electron uptake by *P. aestuarii* in the illuminated cathodic chamber [63]. The outer membrane porin–cytochrome *c* system of *G. sulfurreducens* was shown to be essential for DIET [54]. A recent study based on the electrochemical in situ Fourier transform infrared (FTIR) spectroscopy suggested that outer membrane-associated redox-active proteins, such as cytochrome *c* may be utilized by *P. aestuarii* [63], however, the precise mechanism of electron uptake awaits elucidation.

Sulfur-oxidizing chemoautotrophs

Microbial sulfur oxidation is an important biogeochemical process in modern marine ecosystems and may have been critical in ancient euxinic environments [86, 91, 101]. Evidence for sulfur-dependent chemolithoautotrophic metabolic activity dates back nearly 3.4 billion years [147]. Sulfur-oxidizing bacteria have the metabolic capability to oxidize inorganic forms of sulfur, typically sulfide (H_2S/HS^-), coupled to the reduction of oxygen (O_2) or nitrate (NO_3^-) [46]. The majority of sulfur oxidizers are autotrophs and use reduced sulfur species as electron donors for carbon fixation [46]. Thus, sulfur oxidizers represent an important link in the biogeochemical carbon cycle in oxygen-poor, sulfide-rich environments, such as oxygen minimum zones, marine sediments, and hydrothermal systems [1, 21, 31, 57, 95, 134, 154].

Slowly coming to light is the role of solid substrates for energy flow in sulfur-oxidizing marine sediment microbial communities [82, 83, 123]. Sulfur-oxidizing chemoautotrophs utilize a range of solid substrates in the natural environment, including elemental sulfur (S^0), metallic iron (Fe^0), and reduced iron minerals [82, 123]. Several recent studies have utilized bioelectrochemical approaches to investigate the diversity of mineral-oxidizing microbes in marine sediments [49, 82, 83, 123, 138]. These studies revealed a diversity of bacteria capable of EEU from electrodes over a range of redox potentials [82, 83]. Sulfur-oxidizing chemoautotrophs are known to encode the CBB cycle [12], however, a detailed physiological analysis of EEU in these chemoautotrophs is still lacking. Electrochemical approaches have also been used to isolate sulfur-oxidizing bacteria, including *Thioclava electrotropha* ElOx9, which can utilize electrodes for nitrate reduction and S^0 for carbon fixation [25]. Many members of the *Thioclava* genus are known to assimilate inorganic carbon via CBB cycle [137], however, it is unclear whether *Thioclava electrotropha* ElOx9 can utilize electrodes for carbon fixation [74].

Characterization of the EEU pathways in sulfur oxidizers has been limited to electrochemical studies, because detailed genetic and biochemical work is limited by a lack of organisms in pure culture. Cyclic voltammetry of sulfur and iron-oxidizing bacteria isolated from sediments has revealed a wide range of midpoint potentials that could represent redox-active proteins involved in extracellular electron transfer [82, 123]. Interestingly, electrochemical studies of marine sediment microbes show that iron-oxidizing bacteria have lower (more reduced) midpoint potentials than sulfur oxidizers

[82]. This could indicate divergent molecular pathways for EEU that enable niche differentiation. Detailed comparative genomic, biochemical, and genetic studies are needed to elucidate the molecular pathways that sulfur oxidizers utilize to access electrons from solid substrates.

Biotechnological implications of extracellular electron uptake

The ability of EEU autotrophs to capture and sequester carbon using electricity opens opportunities to develop bioelectrochemical technologies that address the global rise of greenhouse gas emissions [94, 127]. Of particular interest is the ability of these microbes to drive electrosynthesis, where value-added chemical commodities are produced from CO_2 and electricity [76, 107, 132]. Microbial electrosynthesis has been exploited in both chemoautotrophic and photoautotrophic microbes to produce multicarbon chemical commodities [113, 118, 142]. The major bottleneck for widespread use of EEU capable autotrophs for biotechnology is the lack of genetic engineering tools to manipulate these organisms [113].

The current microbial electrosynthesis technologies are primarily focused on the use of acetogens (reviewed in [113]). Microbial electrosynthesis using photoautotrophs is an emerging field. Recent studies of photoautotrophs have advanced our understanding of the molecular mechanisms and the physiology of how electrons from cathodes are utilized for energy transduction and biomass production [11, 52, 53]. Lastly, the rate of electron uptake by microbes directly depends on the total amount and the electron-transfer efficiency of the protein electron–conduits they encode [52, 104]. Although the native EEU capacity of most characterized microbes is limited, it could be improved by genetic engineering. For example, further development of engineered chassis microorganisms with overexpression of either native or heterologous electron–conduit systems could lead to higher electron transfer efficiencies. This could bypass electron-transfer rate limitations. In addition, the development of metabolic engineering strategies to uncouple the use of electrons to biomass production in the native host could improve the ability to direct fixed carbon towards more specific production of value-added chemical commodities.

Acknowledgements The authors would like to acknowledge financial support from the U.S. Department of Energy to A.B. (Grant Number DESC0014613), the David and Lucile Packard Foundation to A.B. (Grant Number 201563111), the Gordon and Betty Moore Foundation to A.B., the U.S. Department of Defense, Army Research Office to A.B. (Grant Number W911NF-18-1-0037) and the National Science Foundation to A.B.(Grant Number 2021822). M.G. performed this work under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DEAC5207NA27344 (LLNL-JRNL-812309) to A.B. and M.G.

Author contributions DG, MSG, and AB performed the necessary literature search. DG, MSG, and AB wrote the manuscript and did critical reading to shape the manuscript. DG and MSG contributed equally to this work. All authors reviewed and contributed to the final version of the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Agostino V, Rosenbaum MA (2018) Sulfate-reducing electroautotrophs and their applications in bioelectrochemical systems. Front Energy Res 6:55
2. Albers SV, Meyer BH (2011) The archaeal cell envelope. Nat Rev Microbiol 9:414–426
3. Amouric A, Brochier-Armanet C, Johnson DB, Bonnefoy V, Hallberg KB (2011) Phylogenetic and genetic variation among Fe(II)-oxidizing *Acidithiobacilli* supports the view that these comprise multiple species with different ferrous iron oxidation pathways. Microbiology 157:111–122
4. Appia-Ayme C, Guiliani N, Ratouchniak J, Bonnefoy V (1999) Characterization of an operon encoding two c-type cytochromes, an aa(3)-type cytochrome oxidase, and rusticyanin in *Thiobacillus ferrooxidans* ATCC 33020. Appl Environ Microbiol 65:4781–4787
5. Barco RA, Emerson D, Sylvan JB, Orcutt BN, Jacobson Meyers ME, Ramirez GA, Zhong JD, Edwards KJ (2015) New insight into microbial iron oxidation as revealed by the proteomic profile of an obligate iron-oxidizing chemolithoautotroph. Appl Environ Microbiol 81:5927–5937
6. Bartlett KB, Harriss RC (1993) Review and assessment of methane emissions from wetlands. Chemosphere 26:261–320
7. Beckwith CR, Edwards MJ, Lawes M, Shi L, Butt JN, Richardson DJ, Clarke TA (2015) Characterization of MtoD from *Sideroxydans lithotrophicus*: a cytochrome c electron shuttle used in lithoautotrophic growth. Front Microbiol 6:332
8. Beese-Vasbender PF, Nayak S, Erbe A, Stratmann M, Mayrhofer KJJ (2015) Electrochemical characterization of direct electron uptake in electrical microbially influenced corrosion of iron by the lithoautotrophic SRB *Desulfopila corrodens* strain IS4. Electrochim Acta 167:321–329
9. Berg IA, Kockelkorn D, Ramos-Vera WH, Say RF, Zarzycki J, Hugler M, Alber BE, Fuchs G (2010) Autotrophic carbon fixation in archaea. Nat Rev Microbiol 8:447–460
10. Bird LJ, Bonnefoy V, Newman DK (2011) Bioenergetic challenges of microbial iron metabolisms. Trends Microbiol 19:330–340
11. Bird LJ, Saraiva IH, Park S, Calçada EO, Salgueiro CA, Nitschke W, Louro RO, Newman DK (2014) Nonredundant roles for cytochrome c2 and two high-potential iron-sulfur proteins in the photoferrotroph *Rhodopseudomonas palustris* TIE-1. J Bacteriol 196:850–858
12. Boschker HT, Vasquez-Cardenas D, Bolhuis H, Moerdijk-Poortvliet TW, Moodley L (2014) Chemoautotrophic carbon fixation rates and active bacterial communities in intertidal marine sediments. PLoS ONE 9:e101443
13. Bose A, Gardel EJ, Vidoudez C, Parra EA, Girguis PR (2014) Electron uptake by iron-oxidizing phototrophic bacteria. Nat Commun 5:3391

14. Brutinel ED, Gralnick JA (2012) Shuttling happens: soluble flavin mediators of extracellular electron transfer in *Shewanella*. Appl Microbiol Biotechnol 93:41–48
15. Bryce C, Blackwell N, Straub D, Kleindienst S, Kappler A (2019) Draft genome sequence of *Chlorobium* sp. strain N1, a marine Fe(II)-oxidizing green sulfur bacterium. Microbiol Resour Announc 8:e00080–e119
16. Brysch K, Schneider C, Fuchs G, Widdel F (1987) Lithoautotrophic growth of sulfate-reducing bacteria, and description of *Desulfobacterium autotrophicum* gen. nov., sp. nov. Arch Microbiol 148:264–274
17. Buckel W, Thauer RK (2018) Flavin-based electron bifurcation, a new mechanism of biological energy coupling. Chem Rev 118:3862–3886
18. Byrne JM, Klueglein N, Pearce C, Rosso KM, Appel E, Kappler A (2015) Redox cycling of Fe (II) and Fe (III) in magnetite by Fe-metabolizing bacteria. Science 347:1473–1476
19. Camacho A, Walter XA, Picazo A, Zopfi J (2017) Photoferrotrophy: remains of an ancient photosynthesis in modern environments. Front Microbiol 8:323
20. Canfield DE, Rosing MT, Bjerrum C (2006) Early anaerobic metabolisms. Philos Trans R Soc Lond B Biol Sci 361:1819–1834
21. Canfield DE, Stewart FJ, Thamdrup B, De Brabandere L, Dalsgaard T, Delong EF, Revsbech NP, Ulloa O (2010) A cryptic sulfur cycle in oxygen-minimum-zone waters off the Chilean coast. Science 330:1375–1378
22. Cao X, Huang X, Liang P, Boon N, Fan M, Zhang L, Zhang X (2009) A completely anoxic microbial fuel cell using a photobiocathode for cathodic carbon dioxide reduction. Energy Environ Sci 2:498–501
23. Castelle C, Guiral M, Malarte G, Ledgham F, Leroy G, Brugna M, Giudici-Orticoni MT (2008) A new iron-oxidizing/O2-reducing supercomplex spanning both inner and outer membranes, isolated from the extreme acidophile *Acidithiobacillus ferrooxidans*. J Biol Chem 283:25803–25811
24. Chan CS, McAllister SM, Garber A, Hallahan BJ, Rozovsky S (2018) Fe oxidation by a fused cytochrome–porin common to diverse Fe-oxidizing bacteria. bioRxiv:228056
25. Chang R, Bird L, Barr C, Osburn M, Wilbanks E, Nealson K, Rowe A (2018) *Thioclava electrotropha* sp. nov., a versatile electrode and sulfur-oxidizing bacterium from marine sediments. Int J Syst Evol Microbiol 68:1652–1658
26. Chen Y, Suzuki I (2004) Effect of uncouplers on endogenous respiration and ferrous iron oxidation in a chemolithoautotrophic bacterium *Acidithiobacillus* (*Thiobacillus*) *ferrooxidans*. FEMS Microbiol Lett 237:139–145
27. Cheng S, Xing D, Call DF, Logan BE (2009) Direct biological conversion of electrical current into methane by electromethanogenesis. Environ Sci Technol 43:3953–3958
28. Crichton RR, Pierre JL (2001) Old iron, young copper: from Mars to Venus. Biometals 14:99–112
29. Croal LR, Jiao Y, Newman DK (2007) The fox operon from *Rhodobacter* strain SW2 promotes phototrophic Fe(II) oxidation in *Rhodobacter capsulatus* SB1003. J Bacteriol 189:1774–1782
30. Crowe SA, Hahn AS, Morgan-Lang C, Thompson KJ, Simister RL, Lliros M, Hirst M, Hallam SJ (2017) Draft genome sequence of the pelagic photoferrotroph *Chlorobium phaeoferrooxidans*. Genome Announc 5:e01584-16
31. Brune DC (1995) Sulfur compounds as photosynthetic electron donors. In: Blankenship RE, Madigan MT, Bauer CE (eds) Anoxygenic photosynthetic bacteria, vol 2. Springer, Dordrecht, pp 847–870
32. de Bok FA, Plugge CM, Stams AJ (2004) Interspecies electron transfer in methanogenic propionate degrading consortia. Water Res 38:1368–1375
33. de Campos RT, Rosenbaum MA (2014) Microbial electroreduction: screening for new cathodic biocatalysts. ChemElectroChem 1:1916–1922
34. Deng X, Dohmae N, Nealson KH, Hashimoto K, Okamoto A (2018) Multi-heme cytochromes provide a pathway for survival in energy-limited environments. Sci Adv 4:eaao5682
35. Deng X, Okamoto A (2018) Electrode potential dependency of single-cell activity identifies the energetics of slow microbial electron uptake process. Front Microbiol 9:2744
36. Deutzmann JS, Sahin M, Spormann AM (2015) Extracellular enzymes facilitate electron uptake in biocorrosion and bioelectrosynthesis. miBo 6:e00496-00415
37. Dinh HT, Kuever J, Mussmann M, Hassel AW, Stratmann M, Widdel F (2004) Iron corrosion by novel anaerobic microorganisms. Nature 427:829–832
38. Drake HL, Gossner AS, Daniel SL (2008) Old acetogens, new light. Ann N Y Acad Sci 1125:100–128
39. Ehrenreich A, Widdel F (1994) Anaerobic oxidation of ferrous iron by purple bacteria, a new type of phototrophic metabolism. Appl Environ Microbiol 60:4517–4526
40. Emerson D, Field EK, Chertkov O, Davenport KW, Goodwin L, Munk C, Nolan M, Woyke T (2013) Comparative genomics of freshwater Fe-oxidizing bacteria: implications for physiology, ecology, and systematics. Front Microbiol 4:254
41. Emerson D, Moyer C (1997) Isolation and characterization of novel iron-oxidizing bacteria that grow at circumneutral pH. Appl Environ Microbiol 63:4784–4792
42. Emerson D, Rentz JA, Lilburn TG, Davis RE, Aldrich H, Chan C, Moyer CL (2007) A novel lineage of proteobacteria involved in formation of marine Fe-oxidizing microbial mat communities. PLoS ONE 2:e667
43. Enning D, Garrelfs J (2014) Corrosion of iron by sulfate-reducing bacteria: new views of an old problem. Appl Environ Microbiol 80:1226–1236
44. Esparza M, Cardenas JP, Bowien B, Jedlicki E, Holmes DS (2010) Genes and pathways for CO_2 fixation in the obligate, chemolithoautotrophic acidophile, *Acidithiobacillus ferrooxidans,* carbon fixation in *A. ferrooxidans*. BMC Microbiol 10:229
45. Ferguson SJ, Ingledew WJ (2008) Energetic problems faced by micro-organisms growing or surviving on parsimonious energy sources and at acidic pH: I. *Acidithiobacillus ferrooxidans* as a paradigm. Biochim Biophys Acta 1777:1471–1479
46. Friedrich CG, Rother D, Bardischewsky F, Quentmeier A, Fischer J (2001) Oxidation of reduced inorganic sulfur compounds by bacteria: emergence of a common mechanism? Appl Environ Microbiol 67:2873–2882
47. Garber AI, Nealson KH, Okamoto A, McAllister SM, Chan CS, Barco RA, Merino N (2020) FeGenie: a comprehensive tool for the identification of iron genes and iron gene neighborhoods in genome and metagenome assemblies. Front Microbiol 11:37
48. Glasser NR, Kern SE, Newman DK (2014) Phenazine redox cycling enhances anaerobic survival in *Pseudomonas aeruginosa* by facilitating generation of ATP and a proton-motive force. Mol Microbiol 92:399–412
49. Gregoire KP, Glaven SM, Hervey J, Lin B, Tender LM (2014) Enrichment of a high-current density denitrifying microbial biocathode. J Electrochem Soc 161:H3049–H3057
50. Gregory KB, Bond DR, Lovley DR (2004) Graphite electrodes as electron donors for anaerobic respiration. Environ Microbiol 6:596–604
51. Gupta D, Guzman MS, Bose A (2019) Draft genome sequence of a marine photoferrotrophic bacterium, *Rhodovulum robiginosum* DSM 12329^T. Microbiol Resour Announc 8:e01684–e1718
52. Gupta D, Sutherland MC, Rengasamy K, Meacham JM, Kranz RG, Bose A (2019) Photoferrotrophs produce a PioAB electron conduit for extracellular electron uptake. mBio 10:e02668-19

53. Guzman MS, Rengasamy K, Binkley MM, Jones C, Ranaivoarisoa TO, Singh R, Fike DA, Meacham JM, Bose A (2019) Phototrophic extracellular electron uptake is linked to carbon dioxide fixation in the bacterium *Rhodopseudomonas palustris*. Nat Commun 10:1355
54. Ha PT, Lindemann SR, Shi L, Dohnalkova AC, Fredrickson JK, Madigan MT, Beyenal H (2017) Syntrophic anaerobic photosynthesis via direct interspecies electron transfer. Nat Commun 8:13924
55. Hallbeck L, Stahl F, Pedersen K (1993) Phylogeny and phenotypic characterization of the stalk-forming and iron-oxidizing bacterium *Gallionella ferruginea*. J Gen Microbiol 139:1531–1535
56. Han X, Tomaszewski EJ, Sorwat J, Pan Y, Kappler A, Byrne JM (2020) Oxidation of green rust by anoxygenic phototrophic Fe(II)-oxidising bacteria. Geochem Perspect Let 12:52–57
57. Hawley AK, Brewer HM, Norbeck AD, Pasa-Tolic L, Hallam SJ (2014) Metaproteomics reveals differential modes of metabolic coupling among ubiquitous oxygen minimum zone microbes. Proc Natl Acad Sci USA 111:11395–11400
58. He S, Barco RA, Emerson D, Roden EE (2017) Comparative genomic analysis of neutrophilic iron(II) oxidizer genomes for candidate genes in extracellular electron transfer. Front Microbiol 8:1584
59. He S, Tominski C, Kappler A, Behrens S, Roden EE (2016) Metagenomic analyses of the autotrophic Fe(II)-oxidizing, nitrate-reducing enrichment culture KS. Appl Environ Microbiol 82:2656–2668
60. Hedrich S, Schlomann M, Johnson DB (2011) The iron-oxidizing proteobacteria. Microbiology 157:1551–1564
61. Holmes DE, Rotaru AE, Ueki T, Shrestha PM, Ferry JG, Lovley DR (2018) Electron and proton flux for carbon dioxide reduction in *Methanosarcina barkeri* during direct interspecies electron transfer. Front Microbiol 9:3109
62. Holmes DE, Ueki T, Tang HY, Zhou J, Smith JA, Chaput G, Lovley DR (2019) A membrane-bound cytochrome enables *Methanosarcina acetivorans* to conserve energy from extracellular electron transfer. mBio 10:e00789-19
63. Huang L, Liu X, Tang J, Yu L, Zhou S (2019) Electrochemical evidence for direct interspecies electron transfer between *Geobacter sulfurreducens* and *Prosthecochloris aestuarii*. Bioelectrochemistry 127:21–25
64. Igarashi K, Kato S (2017) Extracellular electron transfer in acetogenic bacteria and its application for conversion of carbon dioxide into organic compounds. Appl Microbiol Biotechnol 101:6301–6307
65. Ingledew WJ (1982) *Thiobacillus ferrooxidans*. The bioenergetics of an acidophilic chemolithotroph. Biochim Biophys Acta 683:89–117
66. Ishii S, Kosaka T, Hori K, Hotta Y, Watanabe K (2005) Coaggregation facilitates interspecies hydrogen transfer between *Pelotomaculum thermopropionicum* and *Methanothermobacter thermautotrophicus*. Appl Environ Microbiol 71:7838–7845
67. Ishii S, Kosaka T, Hotta Y, Watanabe K (2006) Simulating the contribution of coaggregation to interspecies hydrogen fluxes in syntrophic methanogenic consortia. Appl Environ Microbiol 72:5093–5096
68. Ishii T, Kawaichi S, Nakagawa H, Hashimoto K, Nakamura R (2015) From chemolithoautotrophs to electrolithoautotrophs: CO_2 fixation by Fe(II)-oxidizing bacteria coupled with direct uptake of electrons from solid electron sources. Front Microbiol 6:994
69. Jansen K, Thauer RK, Widdel F, Fuchs G (1984) Carbon assimilation pathways in sulfate reducing bacteria. Formate, carbon dioxide, carbon monoxide, and acetate assimilation by *Desulfovibrio baarsii*. Arch Microbiol 138:257–262
70. Jeans C, Singer SW, Chan CS, Verberkmoes NC, Shah M, Hettich RL, Banfield JF, Thelen MP (2008) Cytochrome 572 is a conspicuous membrane protein with iron oxidation activity purified directly from a natural acidophilic microbial community. ISME J 2:542–550
71. Jiao Y, Newman DK (2007) The pio operon is essential for phototrophic Fe (II) oxidation in *Rhodopseudomonas palustris* TIE-1. J Bacteriol 189:1765–1773
72. Jorgensen CJ, Jacobsen OS, Elberling B, Aamand J (2009) Microbial oxidation of pyrite coupled to nitrate reduction in anoxic groundwater sediment. Environ Sci Technol 43:4851–4857
73. Kappler A, Newman DK (2004) Formation of Fe (III)-minerals by Fe (II)-oxidizing photoautotrophic bacteria. Geochim Cosmochim 68:1217–1226
74. Karbelkar AA, Rowe AR, El-Naggar MY (2019) An electrochemical investigation of interfacial electron uptake by the sulfur oxidizing bacterium *Thioclava electrotropha* ElOx9. Electrochim Acta 324:134838
75. Kato S, Ohkuma M, Powell DH, Krepski ST, Oshima K, Hattori M, Shapiro N, Woyke T, Chan CS (2015) Comparative genomic insights into ecophysiology of neutrophilic, microaerophilic iron oxidizing bacteria. Front Microbiol 6:1265
76. Kato S, Yumoto I, Kamagata Y (2015) Isolation of acetogenic bacteria that induce biocorrosion by utilizing metallic iron as the sole electron donor. Appl Environ Microbiol 81:67–73
77. Kletzin A, Heimerl T, Flechsler J, van Niftrik L, Rachel R, Klingl A (2015) Cytochromes *c* in Archaea: distribution, maturation, cell architecture, and the special case of *Ignicoccus hospitalis*. Front Microbiol 6:439
78. Knittel K, Boetius A (2009) Anaerobic oxidation of methane: progress with an unknown process. Annu Rev Microbiol 63:311–334
79. Konhauser KO, Hamade T, Raiswell R, Morris RC, Ferris FG, Southam G, Canfield DE (2002) Could bacteria have formed the Precambrian banded iron formations? Geology 30:1079–1082
80. Konhauser KO, Kappler A, Roden EE (2011) Iron in microbial metabolisms. Elements 7:89–93
81. Kotloski NJ, Gralnick JA (2013) Flavin electron shuttles dominate extracellular electron transfer *by Shewanella oneidensis*. mBio 4:e00553-12
82. Lam BR, Barr CR, Rowe AR, Nealson KH (2019) Differences in applied redox potential on cathodes enrich for diverse electrochemically active microbial isolates from a marine sediment. Front Microbiol 10:1979
83. Lam BR, Rowe AR, Nealson KH (2018) Variation in electrode redox potential selects for different microorganisms under cathodic current flow from electrodes in marine sediments. Environ Microbiol 20:2270–2287
84. Lemaire ON, Jespersen M, Wagner T (2020) CO_2-fixation strategies in energy extremophiles: what can we learn from acetogens? Front Microbiol 11:486
85. Liu J, Wang Z, Belchik SM, Edwards MJ, Liu C, Kennedy DW, Merkley ED, Lipton MS, Butt JN, Richardson DJ (2012) Identification and characterization of MtoA: a decaheme c-type cytochrome of the neutrophilic Fe (II)-oxidizing bacterium *Sideroxydans lithotrophicus* ES-1. Front Microbiol 3:37
86. Llorens-Mares T, Yooseph S, Goll J, Hoffman J, Vila-Costa M, Borrego CM, Dupont CL, Casamayor EO (2015) Connecting biodiversity and potential functional role in modern euxinic environments by microbial metagenomics. ISME J 9:1648–1661
87. Logan BE (2009) Exoelectrogenic bacteria that power microbial fuel cells. Nat Rev Microbiol 7:375–381
88. Lovley DR (2008) Extracellular electron transfer: wires, capacitors, iron lungs, and more. Geobiology 6:225–231
89. Lovley DR (2017) Syntrophy goes electric: direct interspecies electron transfer. Annu Rev Microbiol 71:643–664

90. Lovley DR, Nevin KP (2013) Electrobiocommodities: powering microbial production of fuels and commodity chemicals from carbon dioxide with electricity. Curr Opin Biotechnol 24:385–390
91. Luther GW 3rd, Findlay AJ, Macdonald DJ, Owings SM, Hanson TE, Beinart RA, Girguis PR (2011) Thermodynamics and kinetics of sulfide oxidation by oxygen: a look at inorganically controlled reactions and biologically mediated processes in the environment. Front Microbiol 2:62
92. Marshall CW, Ross DE, Handley KM, Weisenhorn PB, Edirisinghe JN, Henry CS, Gilbert JA, May HD, Norman RS (2017) Metabolic reconstruction and modeling microbial electrosynthesis. Sci Rep 7:8391
93. Marsili E, Baron DB, Shikhare ID, Coursolle D, Gralnick JA, Bond DR (2008) *Shewanella* secretes flavins that mediate extracellular electron transfer. Proc Natl Acad Sci USA 105:3968–3973
94. Martin WF, Thauer RK (2017) Energy in ancient metabolism. Cell 168:953–955
95. Mattes TE, Nunn BL, Marshall KT, Proskurowski G, Kelley DS, Kawka OE, Goodlett DR, Hansell DA, Morris RM (2013) Sulfur oxidizers dominate carbon fixation at a biogeochemical hot spot in the dark ocean. ISME J 7:2349–2360
96. Matthews E, Fung I (1987) Methane emission from natural wetlands: Global distribution, area, and environmental characteristics of sources. Glob Biogeochem Cycles 1:61–86
97. McAllister SM, Moore RM, Gartman A, Luther GW, Emerson D, Chan CS (2019) The Fe(II)-oxidizing Zetaproteobacteria: historical, ecological and genomic perspectives. FEMS Microbiol Ecol 95:fiz015
98. McAllister SM, Polson SW, Butterfield DA, Glazer BT, Sylvan JB, Chan CS (2020) Validating the Cyc2 neutrophilic iron oxidation pathway using meta-omics of zetaproteobacteria iron mats at marine hydrothermal vents. mSystems 5:e00553-19
99. McGlynn SE (2017) Energy metabolism during anaerobic methane oxidation in ANME Archaea. Microbes Environ 32:5–13
100. McGlynn SE, Chadwick GL, Kempes CP, Orphan VJ (2015) Single cell activity reveals direct electron transfer in methanotrophic consortia. Nature 526:531–535
101. Meyer KM, Kump LR (2008) Oceanic Euxinia in earth history: causes and consequences. Annu Rev Earth Planet Sci 36:251–288
102. Meyerdierks A, Kube M, Kostadinov I, Teeling H, Glockner FO, Reinhardt R, Amann R (2010) Metagenome and mRNA expression analyses of anaerobic methanotrophic archaea of the ANME-1 group. Environ Microbiol 12:422–439
103. Mishra D, Rhee YH (2014) Microbial leaching of metals from solid industrial wastes. J Microbiol 52:1–7
104. Mishra S, Pirbadian S, Mondal AK, El-Naggar MY, Naaman R (2019) Spin-dependent electron transport through bacterial cell surface multiheme electron conduits. J Am Chem Soc 141:19198–19202
105. Nauhaus K, Treude T, Boetius A, Kruger M (2005) Environmental regulation of the anaerobic oxidation of methane: a comparison of ANME-I and ANME-II communities. Environ Microbiol 7:98–106
106. Nevin KP, Hensley SA, Franks AE, Summers ZM, Ou J, Woodard TL, Snoeyenbos-West OL, Lovley DR (2011) Electrosynthesis of organic compounds from carbon dioxide is catalyzed by a diversity of acetogenic microorganisms. Appl Environ Microbiol 77:2882–2886
107. Nevin KP, Woodard TL, Franks AE, Summers ZM, Lovley DR (2010) Microbial electrosynthesis: feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic compounds. mBio 1:e00103-10
108. Pereira L, Saraiva IH, Oliveira ASF, Soares CM, Louro RO, Frazao C (2017) Molecular structure of FoxE, the putative iron oxidase of *Rhodobacter ferrooxidans* SW2. Biochim Biophys Acta Bioenerg 1858:847–853
109. Peters JW, Beratan DN, Bothner B, Dyer RB, Harwood CS, Heiden ZM, Hille R, Jones AK, King PW, Lu Y, Lubner CE, Minteer SD, Mulder DW, Raugei S, Schut GJ, Seefeldt LC, Tokmina-Lukaszewska M, Zadvornyy OA, Zhang P, Adams MW (2018) A new era for electron bifurcation. Curr Opin Chem Biol 47:32–38
110. Philips J (2019) Extracellular electron uptake by acetogenic bacteria: does H_2 consumption favor the H_2 evolution reaction on a cathode or metallic iron? Front Microbiol 10:2997
111. Philips J, Monballyu E, Georg S, De Paepe K, Prevoteau A, Rabaey K, Arends JBA (2019) An *Acetobacterium* strain isolated with metallic iron as electron donor enhances iron corrosion by a similar mechanism as *Sporomusa sphaeroides*. FEMS Microbiol Ecol 95:fiy222
112. Pierson B, Parenteau M, Griffin B (1999) Phototrophs in high-iron-concentration microbial mats: physiological ecology of phototrophs in an iron-depositing hot spring. Appl Environ Microbiol 65:5474–5483
113. Prevoteau A, Carvajal-Arroyo JM, Ganigue R, Rabaey K (2020) Microbial electrosynthesis from CO_2: forever a promise? Curr Opin Biotechnol 62:48–57
114. Quatrini R, Appia-Ayme C, Denis Y, Jedlicki E, Holmes DS, Bonnefoy V (2009) Extending the models for iron and sulfur oxidation in the extreme acidophile *Acidithiobacillus ferrooxidans*. BMC Genom 10:394
115. Rabaey K, Rodriguez J, Blackall LL, Keller J, Gross P, Batstone D, Verstraete W, Nealson KH (2007) Microbial ecology meets electrochemistry: electricity-driven and driving communities. ISME J 1:9–18
116. Rabaey K, Rozendal RA (2010) Microbial electrosynthesis—revisiting the electrical route for microbial production. Nat Rev Microbiol 8:706–716
117. Ragsdale SW, Pierce E (2008) Acetogenesis and the Wood–Ljungdahl pathway of $CO_{(2)}$ fixation. Biochim Biophys Acta 1784:1873–1898
118. Ranaivoarisoa TO, Singh R, Rengasamy K, Guzman MS, Bose A (2019) Towards sustainable bioplastic production using the photoautotrophic bacterium *Rhodopseudomonas palustris* TIE-1. J Ind Microbiol Biotechnol 46:1401–1417
119. Reeburgh WS (2007) Oceanic methane biogeochemistry. Chem Rev 107:486–513
120. Reguera G, McCarthy KD, Mehta T, Nicoll JS, Tuominen MT, Lovley DR (2005) Extracellular electron transfer via microbial nanowires. Nature 435:1098–1101
121. Ross DE, Flynn JM, Baron DB, Gralnick JA, Bond DR (2011) Towards electrosynthesis in *Shewanella*: energetics of reversing the mtr pathway for reductive metabolism. PLoS ONE 6:e16649
122. Rotaru AE, Shrestha PM, Liu F, Markovaite B, Chen S, Nevin KP, Lovley DR (2014) Direct interspecies electron transfer between *Geobacter metallireducens* and *Methanosarcina barkeri*. Appl Environ Microbiol 80:4599–4605
123. Rowe AR, Chellamuthu P, Lam B, Okamoto A, Nealson KH (2014) Marine sediments microbes capable of electrode oxidation as a surrogate for lithotrophic insoluble substrate metabolism. Front Microbiol 5:784
124. Rowe AR, Xu S, Gardel E, Bose A, Girguis P, Amend JP, El-Naggar MY (2019) Methane-linked mechanisms of electron uptake from cathodes by *Methanosarcina barkeri*. mBio 10:e02448-18
125. Schauder R, Widdel F, Fuchs G (1987) Carbon assimilation pathways in sulfate-reducing bacteria II. Enzymes of a reductive citric acid cycle in the autotrophic *Desulfobacter hydrogenophilus*. Arch Microbiol 148:218–225

126. Scheller S, Yu H, Chadwick GL, McGlynn SE, Orphan VJ (2016) Artificial electron acceptors decouple archaeal methane oxidation from sulfate reduction. Science 351:703–707
127. Schuchmann K, Muller V (2013) Direct and reversible hydrogenation of CO_2 to formate by a bacterial carbon dioxide reductase. Science 342:1382–1385
128. Schuchmann K, Muller V (2014) Autotrophy at the thermodynamic limit of life: a model for energy conservation in acetogenic bacteria. Nat Rev Microbiol 12:809–821
129. Shi L, Dong H, Reguera G, Beyenal H, Lu A, Liu J, Yu HQ, Fredrickson JK (2016) Extracellular electron transfer mechanisms between microorganisms and minerals. Nat Rev Microbiol 14:651–662
130. Shi L, Rosso KM, Zachara JM, Fredrickson JK (2012) Mtr extracellular electron-transfer pathways in Fe(III)-reducing or Fe(II)-oxidizing bacteria: a genomic perspective. Biochem Soc Trans 40:1261–1267
131. Shi L, Squier TC, Zachara JM, Fredrickson JK (2007) Respiration of metal (hydr)oxides by *Shewanella* and *Geobacter*: a key role for multihaem *c*-type cytochromes. Mol Microbiol 65:12–20
132. Shrestha PM, Rotaru AE (2014) Plugging in or going wireless: strategies for interspecies electron transfer. Front Microbiol 5:237
133. Shrestha PM, Rotaru AE, Summers ZM, Shrestha M, Liu F, Lovley DR (2013) Transcriptomic and genetic analysis of direct interspecies electron transfer. Appl Environ Microbiol 79:2397–2404
134. Sievert SM, Hugler M, Taylor CD, Wirsen CO (2008) Sulfur oxidation at deep-sea hydrothermal vents. In: Dahl CFCG (ed) Microbial sulfur metabolism. Springer, Berlin, pp 238–258
135. Skennerton CT, Chourey K, Iyer R, Hettich RL, Tyson GW, Orphan VJ (2017) Methane-fueled syntrophy through extracellular electron transfer: uncovering the genomic traits conserved within diverse bacterial partners of anaerobic methanotrophic Archaea. mBio 8:e00530-17
136. Song J, Kim Y, Lim M, Lee H, Lee JI, Shin W (2011) Microbes as electrochemical CO_2 conversion catalysts. Chemsuschem 4:587–590
137. Sorokin DY, Tourova TP, Spiridonova EM, Rainey FA, Muyzer G (2005) *Thioclava pacifica* gen. nov., sp. nov., a novel facultatively autotrophic, marine, sulfur-oxidizing bacterium from a near-shore sulfidic hydrothermal area. Int J Syst Evol Microbiol 55:1069–1075
138. Strycharz-Glaven SM, Glaven RH, Wang Z, Zhou J, Vora GJ, Tender LM (2013) Electrochemical investigation of a microbial solar cell reveals a nonphotosynthetic biocathode catalyst. Appl Environ Microbiol 79:3933–3942
139. Summers ZM, Fogarty HE, Leang C, Franks AE, Malvankar NS, Lovley DR (2010) Direct exchange of electrons within aggregates of an evolved syntrophic coculture of anaerobic bacteria. Science 330:1413–1415
140. Summers ZM, Gralnick JA, Bond DR (2013) Cultivation of an obligate Fe(II)-oxidizing lithoautotrophic bacterium using electrodes. mBio 4:e00420-12
141. Tremblay P-LF, Zhang T (2019) Accelerated H_2 evolution during microbial electrosynthesis with *Sporomusa ovata*. Catalysts 9:166
142. Tremblay PL, Angenent LT, Zhang T (2017) Extracellular electron uptake: among autotrophs and mediated by surfaces. Trends Biotechnol 35:360–371
143. Tsurumaru H, Ito N, Mori K, Wakai S, Uchiyama T, Iino T, Hosoyama A, Ataku H, Nishijima K, Mise M, Shimizu A, Harada T, Horikawa H, Ichikawa N, Sekigawa T, Jinno K, Tanikawa S, Yamazaki J, Sasaki K, Yamazaki S, Fujita N, Harayama S (2018) An extracellular [NiFe] hydrogenase mediating iron corrosion is encoded in a genetically unstable genomic island in *Methanococcus maripaludis*. Sci Rep 8:15149
144. Valdes J, Pedroso I, Quatrini R, Dodson RJ, Tettelin H, Blake R 2nd, Eisen JA, Holmes DS (2008) *Acidithiobacillus ferrooxidans* metabolism: from genome sequence to industrial applications. BMC Genom 9:597
145. Van Driessche G, Vandenberghe I, Devreese B, Samyn B, Meyer TE, Leigh R, Cusanovich MA, Bartsch RG, Fischer U, Van Beeumen JJ (2003) Amino acid sequences and distribution of high-potential iron-sulfur proteins that donate electrons to the photosynthetic reaction center in phototropic proteobacteria. J Mol Evol 57:181–199
146. Villano M, Aulenta F, Ciucci C, Ferri T, Giuliano A, Majone M (2010) Bioelectrochemical reduction of CO_2 to CH_4 via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture. Bioresour Technol 101:3085–3090
147. Wacey D, Kilburn MR, Saunders M, Cliff J, Brasier MD (2011) Microfossils of sulphur-metabolizing cells in 3.4-billion-year-old rocks of Western Australia. Nat Geosci 4:698–702
148. Wang FP, Zhang Y, Chen Y, He Y, Qi J, Hinrichs KU, Zhang XX, Xiao X, Boon N (2014) Methanotrophic archaea possessing diverging methane-oxidizing and electron-transporting pathways. ISME J 8:1069–1078
149. Wang Y, Kern SE, Newman DK (2010) Endogenous phenazine antibiotics promote anaerobic survival of *Pseudomonas aeruginosa* via extracellular electron transfer. J Bacteriol 192:365–369
150. Wegener G, Krukenberg V, Riedel D, Tegetmeyer HE, Boetius A (2015) Intercellular wiring enables electron transfer between methanotrophic archaea and bacteria. Nature 526:587–590
151. Wegener G, Krukenberg V, Ruff SE, Kellermann MY, Knittel K (2016) Metabolic capabilities of microorganisms involved in and associated with the anaerobic oxidation of methane. Front Microbiol 7:46
152. Widdel F, Schnell S, Heising S, Ehrenreich A, Assmus B, Schink B (1993) Ferrous iron oxidation by anoxygenic phototrophic bacteria. Nature 362:834–836
153. Xiong J, Fischer WM, Inoue K, Nakahara M, Bauer CE (2000) Molecular evidence for the early evolution of photosynthesis. Science 289:1724–1730
154. Yamamoto M, Takai K (2011) Sulfur metabolisms in epsilon- and gamma-proteobacteria in deep-sea hydrothermal fields. Front Microbiol 2:192
155. Yarzabal A, Appia-Ayme C, Ratouchniak J, Bonnefoy V (2004) Regulation of the expression of the *Acidithiobacillus ferrooxidans* rus operon encoding two cytochromes *c*, a cytochrome oxidase and rusticyanin. Microbiology 150:2113–2123
156. Yarzabal A, Brasseur G, Ratouchniak J, Lund K, Lemesle-Meunier D, DeMoss JA, Bonnefoy V (2002) The high-molecular-weight cytochrome *c* Cyc2 of *Acidithiobacillus ferrooxidans* is an outer membrane protein. J Bacteriol 184:313–317
157. Yee MO, Rotaru AE (2020) Extracellular electron uptake in Methanosarcinales is independent of multiheme *c*-type cytochromes. Sci Rep 10:372
158. Yee MO, Snoeyenbos-West OL, Thamdrup B, Ottosen LDM, Rotaru A-E (2019) Extracellular electron uptake by two *Methanosarcina* species. Front Energy Res 7:458091
159. Zaybak Z, Logan BE, Pisciotta JM (2018) Electrotrophic activity and electrosynthetic acetate production by *Desulfobacterium autotrophicum* HRM2. Bioelectrochemistry 123:150–155