Chapter 6
Electricity-Driven Microbial Factory for Value-Added Resources Recovery from Waste Streams

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Abstract Over the past few decades, there is a paradigm shift towards recovering value-added products from contaminated water bodies due to the high cost and energy consumption associated with their treatment and disposal. Microbial electrochemical technologies, including electrofermentation (EF), represent a promising option for the production of a wide range of useful products from waste streams. EF technology holds a great promise to improve the output of traditional fermentation by controlling the microbial metabolism through regulating the intracellular and extracellular redox balance, leading to produce chemicals of interest with improved selectivity, specificity, and product recovery. This chapter provides a state-of-the-art analysis for the recent research advancement and technology development. This chapter also discusses the possible microbial community interactions and how it might affect the overall efficiency of EF systems. An overview is given on the integration possibilities of EF with the existing wastewater treatment process that most likely will lead to successful utilization of waste streams and biomass treatment towards developing value-added biorefinery for sustainable circular economy.

6.1 Background

The global energy demand is currently about 13,864 million tons of oil equivalent (Mtoe) annually with over 85% of this demand is being provided from fossil fuels combustion (BP 2019), leading to ~35 gigatons of carbon dioxide (CO_2) emission released into the atmosphere (Dowell et al. 2017; IPCC 2014). Replacing the current means for energy production with more sustainable, carbon-neutral energy sources

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Fig. 6.1 Anaerobic food web, which involves several groups of microorganisms to mediate the biotransformation of complex waste streams into value-added products (Adopted from Mahmoud 2016)
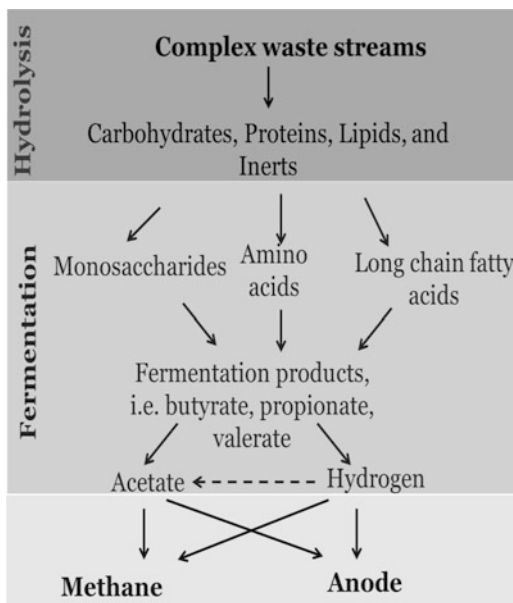
remains a challenge that is facing our society (Brockway et al. 2019; Liu and Rajagopal 2019). Fortunately, this demand can be met from the bioconversion of waste streams to value-added products, such as biochemicals and biofuels. For example, approximately 2.2 million m^3 of wastewater and 2 billion tons of municipal solid waste (MSW) are globally released to the environment every year (Kaza et al. 2018; WWAP (United Nations World Water Assessment Programme) 2017). The release of these potentially harmful waste streams into environment without proper treatment has been a serious cause for concern over the past few decades. Therefore, converting waste streams into various forms of renewable energy creates a "win-win" scenario that solves a wicked waste-management challenge, reduces the cost associated with conventional waste streams treatment, produces renewable energy, and recovers value-added products (Rittmann 2008). Theoretically, energy produced from organic-rich waste streams is approximately a few order of magnitude higher than energy required for wastewater treatment processes (Dubrawski et al. 2019; Logan and Rabaey 2012; Heidrich et al. 2011).

One option for bioenergy production from waste streams is the "anaerobic digestion (AD)," in which different microbial groups convert complex organic compounds under strict anaerobic condition to organic acids and hydrogen gas (H_2), which are subsequently consumed by methanogens to generate methane gas (CH_4) (Fig. 6.1) (Li et al. 2015; Metcalf and Eddy 2003; Rittmann and McCarty 2001). Despite the benefit of producing CH_4 from waste streams digestion, the low conversion yield of CH_4 to electricity (i.e., 30–40%) limits the application of AD to treat low- and medium-strength wastewater. In addition, AD technology is susceptible to process instability and low biogas production, mainly due to the low organic

contents in donor substrates, organic acids accumulation, decrease in the reactor pH, and/or high-level of free ammonia (Mao et al. 2015; Rajagopal et al. 2013; Chen et al. 2008). Thus, AD has often been used to stabilize concentrated waste streams, such as waste activated sludge generated during aerobic domestic wastewater treatment and food wastes (Peccia and Westerhoff 2015; McCarty et al. 2011). Although the coupling of aerobic treatment of wastewater with anaerobic stabilization of waste activated sludge to generate biogas seems to be beneficial, this integration allows only a tiny fraction of this organic matter to be recovered, making the current wastewater treatment practices energy-negative processes (McCarty et al. 2011).

A more recent technology for waste valorization is the "microbial electrochemical technologies (METs)," which are unique platforms that utilize electrochemically-active bacteria (EAB) to catalyze bioelectrochemical reactions. EAB have the capability to exchange electrons beyond their outermost membranes with an electron acceptor (i.e., anode) or an electron donor (i.e., cathode), leading to convert organic compounds into electricity, methane, hydrogen, hydrogen peroxide, or other value-added products (Zou and He 2018; Malvankar and Lovley 2014; Rittmann 2008; Lovley 2008). Despite the growing interest in METs research, only a few studies have addressed the scaling-up of METs with the majority of published research were performed using laboratory-scale MET reactors (i.e., $\ll 1$ liter) (Heidrich et al. 2013; Cusick et al. 2011; Logan 2010). Therefore, the main challenge to commercialize the METs is to improve the electron recovery and the productivity of value-added products, while reducing its high capital, and operation and maintenance (O&M) cost, especially when complex waste streams used as donor substrates (Logan 2010; Rittmann 2008).

Similar to the biodegradation of complex organic matter in AD (Fig. 6.1), the biodegradation of organic matter in METs must be occurred through a cascade of anaerobic reactions, including fermentation and anode respiration. Given that EAB have limited ecological capability to consume a limited number of donor substrates (such as acetate), fermentation represents a crucial step to generate simple products that EAB can efficiently consume (Pant et al. 2010). For example, Ge et al. (2014) showed that the energy recovery of MET systems was inversely proportional to the degree of substrate complexity (expressed as chemical oxygen demand (COD)). They observed that the highest energy recovery was achieved when acetate used as the main sole donor substrate (i.e., 0.40 kWh/kg$_{COD}$ compared to only 0.17 kWh/kg$_{COD}$ for domestic wastewater and 0.04 kWh/kg$_{COD}$ for industrial wastewater). The main cause for this low energy recovery, especially for substrate of low solid contents (e.g., landfill leachate), is the inhibition of fermentation not anode respiration (Mahmoud et al. 2016). Despite the fact that fermentation and anode respiration can be occurred in the same reactor (Mahmoud et al. 2014), the integration of METs with anaerobic digestion to perform some or the majority of fermentation in a separate reactor seems to be beneficial for METs (Katuri et al. 2019; Escapa et al. 2016; Mahmoud et al. 2014).

6.2 Fermentation as an Essential Step in Wastewater Biodegradation

Fermentation represents a crucial step in anaerobic food web, in which soluble organic matter (i.e., the products of particulate organic matter hydrolysis) is converted to organic acids, alcohols, and H_2 (Temudo et al. 2007; Bolzonella et al. 2005). It is considered a central step whether the final product is CH_4 in AD, electric current or H_2 in METs (Rittmann 2008). The hallmark of the fermentation process is that fermenting bacteria extract energy from biodegradable donor substrates without the need of external electron acceptors (e.g., nitrate and oxygen), where the electron acceptors are originated from the initial donor substrates. Fermentation often relies on substrate-level phosphorylation to drive adenosine triphosphate (ATP) generation (Rodríguez et al. 2006; Metcalf and Eddy 2003; Rittmann and McCarty 2001). Thus, fermentation involves a rearrangement of donor substrate molecules into simpler products (i.e., organic acids, alcohols, and H_2) (Fig. 6.2).

Considering the mixed-culture fermentation of glucose, one mole of glucose could theoretically produce 2 moles of acetate, and 4 moles of H_2 (Eq. (6.1)) that its partial pressure should be maintained at a very low level in order to make fermentation thermodynamically favorable (Mahmoud et al. 2017; Angelidaki et al. 2011; Rodríguez et al. 2006; Thauer et al. 1977).
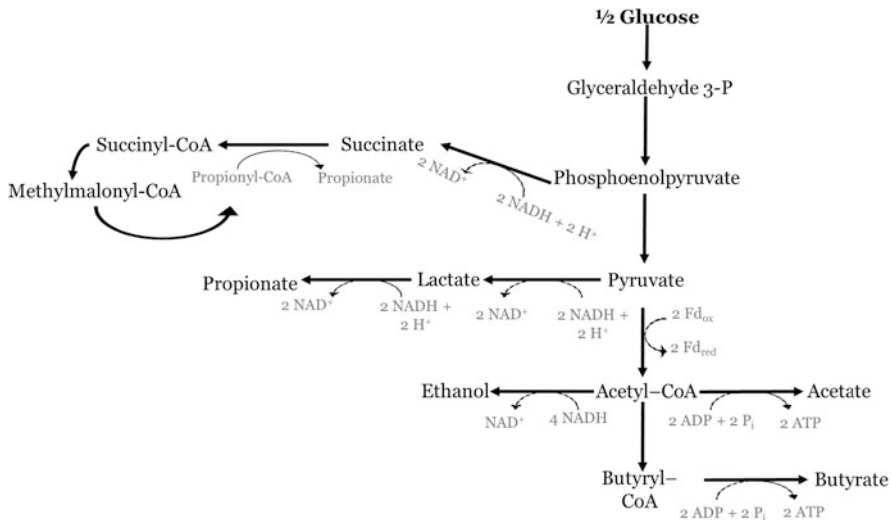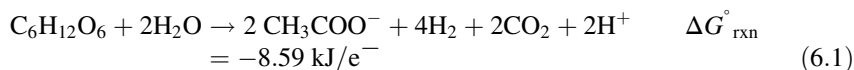

Fig. 6.2 Selected fermentation pathways involved in the mixed-culture glucose fermentation

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2\ CH_3COO^- + 4H_2 + 2CO_2 + 2H^+ \qquad \Delta G^{\circ}{}_{rxn}$$
$$= -8.59\ kJ/e^- \tag{6.1}$$

In order to make fermentation thermodynamically feasible, hydrogen partial pressure must be maintained at a low level (Hallenbeck 2009; Stams and Plugge 2009; McInerney et al. 2008). However, increasing the hydrogen partial pressure would induce a metabolic shift in the fermentation pathways and stoichiometry towards producing more reduced organic acids (e.g., butyrate, lactate, and propionate) instead of producing acetate and H_2. The main reason for this detouring is that at high hydrogen partial pressure microbes tend to replenish the NAD^+ and oxidized ferredoxin pools to continue fermentation, resulting in production of more reduced organic acids (Angenent et al. 2004).

Another major challenge for fermentations is that the product spectrum as well as microbial population structure and diversity can be significantly altered by changing the operating conditions, including pH (Lu et al. 2011; Metcalf and Eddy 2003), organic matter loading (Temudo et al. 2008), the degree of substrate complexity (Saint-amans et al. 2001; Himmi et al. 2000), the presence of inhibitory compounds (Mahmoud et al. 2017), and temperature (Batstone et al. 2002). For instance, Velasquez-Orta et al. (2011) showed that the microbial fuel cell (MFC) performance, in terms of COD removal and power density generation, was significantly affected by the degree of substrate complexity. The highest power density was reported when acetate used as the sole donor substrate (99 ± 2 mW/m^2) compared to only 4 ± 2 mW/m^2 for starch, mainly due to that different initial donor substrates have distinct degree of substrate degradation and fermentation pathways. In another study, Zhang et al. (2014) revealed that the microbial community structure of AD bioreactors significantly changes as a function of the influent donor substrate composition, probably due to the inability of many microbes to use certain substrates to grow, leading to a dramatic change in mixed-culture community structure towards species that have the ability to consume these substrates.
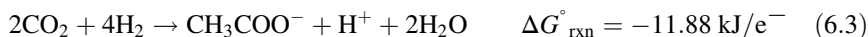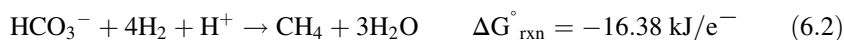
6.3 Overcoming the Fermentation Bottlenecks Through Electricity-Driven Fermentation

In an early review, Rabaey and Rozendal (2010) discussed the possibility to alter the fermentation pathways towards the production of targeted chemicals and bioproducts by inserting polarized electrodes in the bulk solution of AD reactors, which was later called "electrofermentation (EF)" (Rabaey and Rozendal 2010). The role of polarized electrodes is to provide an external source of either oxidizing or reducing power, leading to stimulate microbial metabolism in traditional fermentation bioreactor towards producing targeted chemicals and enhancing the microbial growth (Agler et al. 2011). In this platform, the supplied electric current allows the organic matter fermentation to proceed under imbalanced redox conditions by

altering the extracellular and intracellular NAD⁺/NADH balance and oxidation-reduction potential (ORP) (Moscoviz et al. 2016).

In anodic EF, organic-rich substrates (e.g., carbohydrate and protein), which are the main source of electrons and energy, are fermented into more oxidized final products. In this case, the anode acts as the terminal electron acceptor. In contrast, the working electrode in cathodic EF (i.e., cathode) supplies electrons to the microbial cells, leading to convert the initial substrates into more reduced final products (Kracke and Krömer 2014).

EF systems have been commonly used to improve the production of a wide spectrum of value-added products from different waste streams (Table 6.1). Similar to AD, the complex organic matter in METs is biodegraded through a cascade of bioelectrochemical reactions under strict anaerobic condition. First, the particulate organic matter is hydrolyzed to soluble monomer, which is then converted into organic acids, alcohols, and H_2 by fermenting bacteria. Then, the majority of fermentation by-products are further converted into acetate and H_2. Finally, acetate and H_2 are consumed by either EAB (the desired pathway) or methanogens to generate CH_4 (the undesired pathway) (McCarty et al. 2011; Parameswaran et al. 2010; Thauer et al. 2008; Rittmann and McCarty 2001). Generally, there are two main H_2-consumers in the anode of MET systems rather than EAB: hydrogenotrophic methanogens and homoacetogens (Mahmoud et al. 2017). Hydrogenotrophic methanogens consume H_2 as the main donor substrate to produce CH_4 (Eq. (6.2)) (Stams and Plugge 2009; Thauer et al. 2008), while homoacetogens also consume H_2 to yield acetate (Eq. (6.3)) (Schuchmann and Müller 2014). Thus, it is a challenge to minimize the conversion of H_2 to CH_4, in the presence of hydrogenotrophic methanogens; however, there are several attempts to limit or inhibit the activity of methanogens, such as using chemical inhibitors (Zhu et al. 2015; Parameswaran et al. 2010), employing active harvesting of H_2 (Lu et al. 2016), altering operational conditions (Mahmoud et al. 2017), and genetically modifying EAB (Awate et al. 2017).

$$HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O \qquad \Delta G^{°}_{rxn} = -16.38 \text{ kJ/e}^- \qquad (6.2)$$

$$2CO_2 + 4H_2 \rightarrow CH_3COO^- + H^+ + 2H_2O \qquad \Delta G^{°}_{rxn} = -11.88 \text{ kJ/e}^- \qquad (6.3)$$

Recently, Zhao et al. (2015) studied the role of polarized electrodes for enhancing CH_4 production in AD bioreactor fed with waste activated sludge. Despite the obvious increase in CH_4 production compared to control experiments (without polarized anodes), mass balance revealed that >50% of CH_4 production was originated from unknown pathway. Microbial community analysis as well as fluorescence in situ hybridization (FISH) revealed the dominance of *Methanosaeta* and *Geobacter* species in electric-anaerobic sludge digester bioreactors. Owing to the increase in biofilm conductivity, they concluded that polarized anode facilitated organic matter degradation and electron exchange between methanogens and

Table 6.1 Application of EF for improving the value-added products recovery from wastes streams

EF reactor architecture (reactor volume)	Mode of operation	Substrate	Donor substrate concentration	Inoculum	Electrode type	Applied potential	Organic matter removal	Desired final product	Reference
(1) Anodic EF									
Single-chamber reactor (1 L)	Batch	Composite food waste	10 g COD/L	Mixed-culture	Graphite	-0.6 V[a]	57%	Mixed organic acids	Sravan et al. (2018)
Single-chamber reactor (0.126 L)	Batch	Fermented food waste	N.A.[b]	Mixed-culture	Carbon fiber	$+0.8$ V[b]	70–87%	H_2 and CH_4	Jia et al. (2020)
Dual-chamber reactor (16 mL)	Continuous	Pre-treated switchgrass waste	0.026 g /L	Mixed-culture	Carbon felt	-0.005[a]	Up to 74.2%	H_2	Lewis and Borole (2016)
Dual-chamber reactor (0.32 L)	Continuous	Pre-treated landfill leachate	1.23 g COD/L	Mixed-culture	Graphite rods	-0.046[a]	28%	H_2	Mahmoud et al. (2016)
Dual-chamber reactor (90 mL)	Batch	Glycerol	Up to 100 g glycerol/L	*G. sulfurreducens* + *C. cellobioparum*	N.A.[b]	$+0.445$[a]	100%	Mixed product (i.e., acetate, lactate, ethanol, and H_2)	Speers et al. (2014)
Dual-chamber reactor (0.2 L)	Batch	A mixture of phenolic compounds	200–1200 mg/L	Mixed-culture	Carbon felt	$+0.6$[c]	49–61%	H_2	Zeng et al. (2015)
Dual-chamber reactor (25 mL)	Batch	Glycerol	1 mmol glyc-erol/L	Engineered *E. coli*	Graphite felt	$+0.2$[a]	80%	Ethanol and acetate	Sturm-Richter et al. (2015)
Dual-chamber reactor (0.31 L)	Batch	Glycerol	11.05 g glyc-erol/L	Recombinant *Klebsiella pneumoniae* L17	Carbon cloth	$+0.705$[a]	100%	3-hydroxypropionic acid	Kim et al. (2017)
Dual-chamber reactor (0.145 L)	Batch	Dye wastewater	Up to 300 mg dye/L	Mixed-culture	Graphite brush	$+ 0.8$ V[c]	Up to 96%	H_2	Hou et al. (2017)
Dual-chamber reactor (88 L)	Continuous	Domestic wastewater	~400 mg COD/L	Mixed-culture	Cardon felt	$+1.1$ V[c]	34%	H_2	Heidrich et al. (2013)

Table 6.1 (continued)

EF reactor architecture (reactor volume)	Mode of operation	Substrate	Donor substrate concentration	Inoculum	Electrode type	Applied potential	Organic matter removal	Desired final product	Reference
(2) Cathodic EF									
Dual-chamber reactor (0.9 L)	Batch	Glycerol	17.5 g glycerol/L	Mixed-culture + *G. sulfurreducens*	Planar graphite	-0.656^a	100%	1,3-propanediol	Moscoviz et al. (2018)
Dual-chamber reactor (0.86 L)	Continuous	H_2	N.A.[b]	Mixed-culture	Graphite granules	-0.850^a	N.A.[b]	CH_4	Villano et al. (2011)
Dual-chamber reactor (0.45 L)	Batch	Glycerol	0.3 mmol/L	*Clostridium pasteurianum* DSM 525	Graphite felt	$+0.045^a$	100%	Butanol and 1,3-propanediol	Choi et al. (2014)
Dual-chamber reactor (0.45 L)	Batch	Sucrose	5 g Sucrose /L	*Clostridium tyrobutyricum*	Graphite felt	-0.545^a	100%	Butyrate	Choi et al. (2012)
Dual-chamber reactor (0.65 L)	Batch	Glucose	3 g glucose/L	Mixed-culture	Graphite plate	—	76.52%	Polyhydroxyalkanoates	Srikanth et al. (2012)
Dual-chamber reactor (0.25 L)	Batch	Glucose	3 g glucose/L	*Corynebacteriumglutamicum*	Graphite plate	-0.401^a	100%	Lactate	Sasaki et al. (2014)
Dual-chamber reactor (0.87 L)	Batch	Acetate	50 mmol/L	Mixed-culture	Graphite felt	-0.433^a	100%	Ethanol, butyrate, propionate, and methane	Steinbusch et al. (2010)
Dual-chamber reactor (0.28 L)	Batch	Corncob hydrolysate	15 g sugar/L	*A. Succinogenes* NJ113	Carbon felt	-0.8^a	N.A.[b]	Succinate	Zhao et al. (2016)
Dual-chamber reactor (0.1 L)	Batch	Glycerol	20 g glycerol/L	*Klebsiella pneumoniae*	Graphite felt	-0.45^a	~60%	Ethanol, succinate, lactate, acetate, and 1,3-propanediol	Harrington et al. (2015)

[a]Potential is reported versus standard hydrogen electrode (SHE)
[b]*N.A.* not available
[c]Potential applied between anode and cathode

Geobacter species. In more recent study, Luo et al. (2016) documented the positive role of polarized electrode for enhancing CH_4 production under ammonia stress.

Taken together, these available laboratory-scale studies demonstrate that EF platform opens up new opportunities to integrate METs with the existing AD technology in order to solve the problems associated with conventional AD technology, such as low product yield, slow hydrolysis/fermentation rate (Park et al. 2018), the requirement of long sludge and hydraulic retention times (Song et al. 2016), and the process instability at low temperature (Liu et al. 2016).

In cathodic EF, the electrode acts as the source of electrons to stimulate EF towards production of more reduced final products, including 1,3-propanediol (1,3-PDO), butanol, and polyhydroxyalkanoates (PHA), with high purity and rate (Xue et al. 2017; Moscoviz et al. 2016; Kracke and Krömer 2014). For instance, Choi et al. (2014) showed that a positive working potential (i.e., +0.045 V vs. standard hydrogen electrode (SHE)) triggered a metabolic shift in *Clostridium pasteurianum* towards production of NADH-consuming metabolite, such as 1,3-PDO from glycerol fermentation and butanol from glucose. More recently, there are efforts to use mixed-culture microbial community for glycerol electrofermentation to selectively produce 1,3-PDO (Roume et al. 2016; Xafenias et al. 2015; Zhou et al. 2013).

Although the use of electric current has been proved to be effective tool to drive the microbial, allowing the production of targeted chemicals of interest, it seems to be a challenge to build successful mixed-culture microbiomes that are resilient to improve the EF selectivity and specificity (Schievano et al. 2016). Dennis et al. (2013) revealed that change in microbial community structure was significantly associated with change in electrofermentation pathway of glycerol and product spectrum. Zhou et al. (2015) observed that the sharp decrease of 1,3-PDO production from glycerol over long time of operation (>150 days) was associated with loss of the dominant *Citrobacter* spp.

Polyhydroxyalkanoates (PHA) is another targeted chemical that can be produced during the cathodic EF of glucose. In a proof-of-concept study, Srikanth et al. (2012) observed high accumulation of PHA (19% of dry cell weight) with high hydroxybutyrate concentration(~89%) by providing a microaerophilic environment in the cathode of an MET with glucose as the sole carbon source.

6.4 Towards Building Successful Microbiome: Teamwork or Coexistence?

Despite the fact that the EET mechanism in METs has not yet been fully elucidated, there are 2 main mechanisms through which EAB can exchange electrons with electrodes: direct electron transfer and indirect (or mediated) electron transfer (Fig. 6.3) (Torres et al. 2010). Indirect electron transfer relies on redox active shuttles that transfer electrons between EAB and solid surfaces by altering their oxidation states. The extracellular shuttles can be either a secondary microbial metabolite (e.g.,
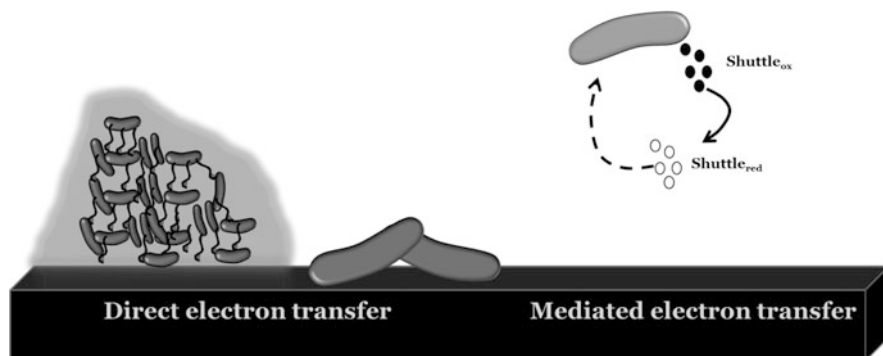
Fig. 6.3 Proposed electron transport mechanisms used by EAB (Adopted from Mahmoud 2016; Torres et al. 2010)

phenazine and flavins) or synthetic molecules (e.g., Anthraquinone-2,6-disulfonic acid, neutral red, and cobalt(III) sepulchrate) (Kracke et al. 2018; Torres et al. 2010; Marsili et al. 2008; Emde and Schink 1990). For direct electron transfer, EAB community has the ability to exchange electrons with solid surfaces via direct contact of redox proteins embedded within the EAB outer membrane (e.g., nanowires) (Malvankar and Lovley 2014; Lovley 2008). These mechanisms have been commonly postulated in anodic and cathodic EF systems (Moscoviz et al. 2016; Torres et al. 2010; Rabaey and Rozendal 2010). Although the study of EET in the anode of METs in early studies has focused only on two Gram-negative, mesophilic EAB: *Shewanella oneidensis* MR-1 and *Geobacter sulfurreducens*, there are so far over 100 isolated EAB that have the ability to transfer the electron to/from solid surfaces (Logan et al. 2019; Doyle and Marsili 2018).

EAB community performing indirect electron transfer (e.g., *S. oneidensis* MR-1) is often characterized with low current density generation (i.e., ≤ 1 A/m^2) mainly due to the slow diffusion of redox shuttles, although they are capable of using fermentable donor substrates, such as glucose, as the main source of energy and electrons. On the other hand, EAB community performing respiration via solid-conductive mechanism (e.g., *G. sulfurreducens*) are capable of producing much higher current density; however, their metabolic capability is limited to only consume simple substrates, including acetate and H$_2$ (Torres et al. 2010; Marsili et al. 2008). In order to overcome this limited metabolic capability, Speers et al. (2014) proposed a successful strategy to use a co-culture of an EAB (*G. sulfurreducens*) and a fermenting bacterium (*Clostridium cellobioparum*) to enhance glycerol fermentation into ethanol. Interestingly, Lusk et al. (2015) used a pure-culture thermophilic bacterium—*Thermoanaerobacter pseudethanolicus*—that has the ability to ferment complex donor substrates (e.g., xylose, glucose, and cellobiose) and perform anode respiration without the addition of redox mediators.

Despite the benefits of using pure cultures in EF systems for higher selectivity and specificity of fermentation reactions, mixed-culture EF systems may be advantageous to simplify the fermentation process. Owing to the high robustness and

functional stability of mixed-culture microbial community compared to pure cultures, mixed-culture EF systems can handle a wide range of complex waste streams, such as real wastewater. It was previously demonstrated in different MET configurations that EAB rely on fermenting bacteria to provide their "fuel" by converting complex organic matter into simple donor substrates (Logan et al. 2019; Mahmoud et al. 2017; Parameswaran et al. 2010). These syntrophic interactions—either by mediated interspecies electron transfer (MIET) via the diffusion of electron carriers (i.e., H_2 and formate) (Parameswaran et al. 2010) or direct interspecies electron transfer (DIET) in presence of conductive materials (Lovley 2017)—are required to maintain the concentrations of fermentation by-products below a threshold limit to make the fermentation thermodynamically favorable (Kiely et al. 2011).

Although methanogens represent the main trophic guild in anaerobic digesters to produce CH_4 from organic wastes, methanogens represent undesired competitors for EAB, since they can compete for space and food (Siegert et al. 2015). They can produce CH_4 by two pathways: (1) aceticlastic methanogenesis by oxidizing acetate (Eq. (6.4)) and (2) hydrogenotrophic methanogenesis by oxidizing H_2 (Eq. (6.2)). Owing to the thermodynamic and kinetic advantages of EAB over aceticlastic methanogens, EAB usually outcompete aceticlastic methanogens (Parameswaran et al. 2010; Esteve-Nunéz et al. 2005); hence, they are not a competitor for acetate-consuming EAB. However, hydrogenotrophic methanogens have metabolic advantage over EAB for H_2 consumption, thereby minimizing the possibility of H_2 harvesting or its conversion into another useful product, such as electric current (Mahmoud et al. 2017). Among several possibility to inhibit methanogens, chemical inhibitors (e.g., 2-bromoethanesulfonate) seem to be the most effective option for inhibiting methanogens, although using chemical inhibitors is not practically feasible for industrial applications of EF and other MET as well as they are toxic (Karthikeyan et al. 2017; Mahmoud et al. 2017; Lu et al. 2016; Zhu et al. 2015; Parameswaran et al. 2010; Chae et al. 2010; Freguia et al. 2008).

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \qquad \Delta G^\circ = -3.88 \text{ kJ/e}^- \qquad (6.4)$$
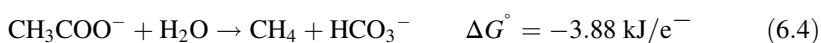
Another potential competitor for EAB is sulfate-reducing bacteria (SRB). Sulfate reduction process in the anodic EF systems is likely to occur, particularly for sulfate-rich organic waste streams, such as food wastewater, petrochemical effluents, and pulp and paper wastewater (Hao et al. 2014). Although there is no comprehensive study showing the impact of sulfate on the performance of EF systems, a recent study revealed the applied current in a microbial electrolysis cell favored sulfate removal from sulfate-rich wastewater (Wang et al. 2017). Their results suggest that EAB can integrate with SRB to remove organic matter and sulfate, although they did not study the effect of sulfate on anode respiration. In another study, Lee et al. (2012) showed that increasing the sulfate concentration had a negative effect on the performance of MFCs as indicated from low power density generation and electron recovery.

Given that nitrate can be reduced in strict anaerobic conditions, it represents a real risk for EAB in the anode of MET reactors, including anodic EF systems. Nitrate reduction by nitrate-reducing bacteria (NRB) (or denitrifiers) is an undesired process, since it would limit the substrate availability for EAB (Sukkasem et al. 2008). For instance, Jin et al. (2019) showed that supplementing the anode of an MFC with nitrate (100 mg-N/L) decreased Coulombic efficiency (CE) by ~2.2-fold (from 63.9% to 29.4%). In another study, Kashima and Regan (2015) studied the impact of nitrate on the efficiency of pure-culture electrochemically-active bacterium (i.e., *Geobacter metallireducens*). The addition of nitrate (10 mM) resulted in a remarkable reduction of CE (from ~78% to ~4%). A likely reason for low CE and electron losses is the competition between EAB and NRB for substrate and space.

6.5 EAB–Electrode Interaction and EF Systems Architecture

So far, the majority of published research were performed using small-scale EF systems. Thus, the successful scaling-up of EF systems (and other MET as well) will greatly depend on the selection of biocompatible electrodes that favor the microbe-electrode interactions as well as the system design and architecture (Logan et al. 2006). The ideal electrodes for EF systems should have: (1) a relatively high electrical conductivity; (2) high chemical stability; (3) low cost; (4) large accessible specific surface area; and (5) high mechanical strength (Hindatu et al. 2017; Xie et al. 2015).

Owing to their biocompatibility, low cost, and high electrical conductivity, carbon-based electrodes, including graphite brush, carbon cloth, graphite felt, carbon brush, granular activated carbon, and carbon fibers, have been widely used for METs research (ElMekawy et al. 2017; Xie et al. 2015). In addition, altering the surface chemistry of electrodes by either adding conductive catalysts (e.g., carbon nanotube, graphene, and iron oxide) or conducting polymers (e.g., polyaniline and hydrogels) has resulted in enhancing the bacterial colonization and microbe-electrode interactions, thereby reducing the surface electron transfer resistance and improving the extracellular electron (EET) rate (Hindatu et al. 2017). Other surface treatment approaches (e.g., acid treatment (Feng et al. 2010), ammonia treatment (Call et al. 2009), surfactant treatment (Guo et al. 2014a), heat treatment (Wang et al. 2009), and flame oxidation (Guo et al. 2014b) have been applied to alter the surface chemistry of electrodes, facilitating the microbe-electrode interaction and enhancing biocompatibility properties of electrodes. In addition, other non-carbon electrodes (e.g., stainless steel, gold, and titanium) have also been used for METs research; however, their small accessible specific surface area and relatively high cost would limit their application for large-scale MET reactors (Fan and Liu 2014; Richter et al. 2008; Dumas et al. 2008).

Most of recent EF studies have paid more attention to understand the fundamental aspects of EF systems rather than the reactor design and architecture. Single-chamber EF system (i.e., without using ion-exchange membranes) seems to be ideal to upgrade the existing AD technologies for wastewater treatment, such as municipal sludge and food-processing wastewater. This approach would enhance the efficiency of AD, while keeping its O&M relatively low. However, if the purpose of EF system is to recover high-purity chemicals, EF should occur in multi-chambered EF systems equipped with of ion-exchange membranes (bipolar membrane, anion-exchange membrane, and cation-exchange membrane). For example, Roume et al. (2016) used a 3-chambered cathodic EF system to enhance the bioelectrochemical reduction of glycerol to 1,3-PDO. Using arrays of selective membranes, they reported a high production yield of 1,3-PDO (i.e., 0.72 mole of 1,3-PDO per 1 mole of glycerol). Similarly, Andersen et al. (2014) revealed that using an anion-exchange membrane remarkably enhanced the extraction and upgrading of short-chain carboxylates into esters during bioelectrochemical fermentation.

6.6 Conclusion and Future Perspectives

EF is an emerging platform that integrates electrochemistry with traditional fermentation. In EF systems, the polarized electrodes can act as either electron acceptor (i.e., anodic EF) or electron donor (i.e., cathodic EF), leading to stimulate microbial metabolism in traditional fermentation bioreactor to produce targeted chemicals with high purity, to enhance microbial growth, to improve the microbial interspecies interactions, and/or to achieve carbon breakdown or chain elongation. Despite the great promise of this hybrid technology, it is still in its infancy. Multidisciplinary studies are required:

1. to understand the microbial community interaction and how it affects the microbial metabolism as well as cultivating new microbial isolates that are capable of improving the selectivity and specificity of EF. Owing to the recent advances in molecular biology and culture-independent tools and techniques, both options seem to be easily achievable,

2. to improve the EF system architecture and design, including the electrode materials and shapes. This remarkably improvement of EF efficiency has to be accompanied with novel reactors design that should have a relatively low cost and high availability,

3. to investigate the possibility of integration with other existing wastewater treatment processes, such as anaerobic digestion, and

4. to find a practical way to improve the extraction of the produced chemicals.

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