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Harvest and utilization of chemical energy in wastes by microbial fuel cell

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Abstract

Organic wastes are now increasingly viewed as a resource of energy that can be harvested by suitable biotechnologies. One promising technology is microbial fuel cell (MFC), which can generate electricity from the degradation of organic pollutants. While the environmental benefits of MFC in waste treatment have been recognized, its potential as an energy producer is not fully understood. Although progresses in material and engineering have greatly improved the power output from MFC, how to efficiently utilize the MFC's energy in real-world scenario remains a challenge. In this review, fundamental understandings on the energy-generating capacity of MFC from real waste treatment are provided and the challenges and opportunities are discussed. The limiting factors restricting the energy output and impairing the long-term reliability of MFC are also analyzed. Several energy storage and in-situ utilization strategies for the management of MFC's energy are proposed, and future research needs for real-world application of this approach are explored.

1. Introduction

Renewable energy sources as sustainable and carbon-neutral alternatives to fossil fuels are highly desirable to alleviate the global energy crisis and environmental deterioration. According to the prediction of the European Renewable Energy Council, approximately half of the global energy supply will come from renewable energy by 2040.[1] Various wastes are potentially a huge renewable energy reservoir due to their abundant availability and rich organic matter contents. Within the last decades, waste management has changed from being a sector primarily focusing on treatment and final disposal to a potential factory of energy and resources.[2]

The bioelectrochemical systems (BESs) are receiving tremendous attention for the energy-efficient treatment of wastes. Microbial fuel cell (MFC) is one typical form of BES that directly converts chemical energy in wastes into electric energy by taking advantage of the synergy between microbial metabolism and a solid electron acceptor. In an MFC, microorganisms oxidize biodegradable organics at anode, releasing electrons and protons. The bacteria that can extracellularly transfer electrons from organics to anode electrode are called exoelectrogens.[3] Electrons flow via an external circuit to cathode and react with protons migrating inside the cell and electron acceptor (Fig. 1). Many oxidants including oxygen (O_2),[4] ferricyanide,[4,5] permanganate,[6] dichromate[7] and persulfate[8] can be used as an electron acceptor. Especially, O_2 is the most commonly used due to its abundance and easy availability in air, low cost and non-toxicity.[9]

MFC could be utilized as a potential alternative to conventional anaerobic digestion. In anaerobic digestion, energy is recovered in the form of methane (CH_4) and/or hydrogen (H_2), but more than 65% energy loss occurs in the process of biogas combustion and conversion into electricity.[10] Moreover, the large quantity of undesirable impurities, such as hydrogen sulfide, in biogas should be removed in order to maintain an efficient operation of electric generator. In comparison, MFC allows a direct transformation of chemical energy (organic matters in waste) into electricity, theoretically affording less energy loss than the multi-step energy transformation needed by anaerobic digestion. MFC does not require gas treatment because the off-gas is mainly composed by carbon dioxide (CO_2) with no useful energy content. Notably, biogenic CO_2 generated from MFC is considered as environmentally neutral and of negligible contribution to global warming.[11] This is a potential advantage over anaerobic digestion, whose off-gas CH_4 contributes to major greenhouse gas emission from biological waste treatment.[12] In addition, considerable environmental benefits can be achieved by the displacement of fossil-fuel based electricity with bioelectricity.[13]

MFC is operated in a way similar to a chemical fuel cell, except that it uses microorganisms as a catalyst at anode. This endows it extra advantages. Unlike chemical fuel cells that utilize only limited types of chemicals as their fuel, MFC is able to produce electricity from an enormous range of low-grade wastes. In addition, chemical fuel cells are usually operated at high temperatures (500 to 1000 °C) and strong acidic or alkaline pH, posing rigid requirements on the reactor materials and adding operational costs.[14] Yet the mild operational conditions with ambient temperature and neutral pH make MFC more reliable and safer.

MFC is a promising technology to combat the existing energy demand and pollution problem. While the environmental benefits of MFC have been recognized to suit a sustainable pattern of waste treatment, its potential as an energy producer has not been well addressed yet. Even though advances in material and engineering have greatly improved the power output from MFC, most of the achievements are obtained with synthetic cultures and pure substrates, rather than real wastes, i.e., complex mixture of organic matters.[15,16] For MFCs used to treat real wastes the primary goal is usually not to achieve a high power output, but to improve organic removal. As a result, the potential of MFC to recover electric energy from real wastes remains not clearly recognized. The successful demonstration of energy self-sufficient MFC necessitates the full exploitation of MFC's energy to harness real waste treatment.[17] Traditionally, MFC is operated with an external resistor, and the maximum power obtained at its optimum external resistance is used to represent its energy-generating capacity. However, in order to harvest actual energy from MFC, the resistor has to be replaced with devices that can capture and store energy. Thus, the maximum power output of MFC can hardly be achieved because of the suboptimal external resistance in practical operation. While tremendous efforts have been devoted to boost the energy-generating capacity of MFC, how to effectively harvest and utilize the energy should be given more attention.

In this review, advances of MFC in the production of electric power from real wastes and the management of MFC energy for practical applications are overviewed. With a critical analysis of the opportunities and challenges of MFC towards the energy harvest from real wastes, this review aims to identity the possible approaches for the virtual utilization of MFC energy, analyze the factors constraining the energy output of MFC, and prospect energy storage and in-situ utilization strategies to bring the MFC technology into real-world application.

2. Energy-generating capacity of MFC

A series of parameters for evaluating the overall energy-generating capacity of MFC have been recommended.[3,18-20] The most widely used parameters are current density and power density, which principally tell how much electricity is produced from MFC. Since electricity generation is usually coupled with waste treatment in MFC, it is necessary to assess the MFC performance in terms of electric energy recovery from waste. Thus, normalized energy recovery (*NER*), Coulombic efficiency (*CE*) and energy-conversion efficiency (*ECE*) should also be taken into consideration.

2.1 Current density and power density

Current density is a commonly used parameter to describe “electricity generation” performance in MFC. It represents the current in terms of unit electrode surface area or reactor volume. Usually current is normalized by the geometric surface area of anode, whereas cathode surface area is sometimes used when the cathode reaction is the rate-limiting step. Thus, the current density is calculated as:

$$I_{An} = \frac{I}{A_{An}} \tag{1}$$

$$I_{Cat} = \frac{I}{A_{Cat}} \tag{2}$$

Similarly, the anodic chamber volume is used to calculate the volumetric current density:

$$I_V = \frac{I}{V_R} \tag{3}$$

where I is the current (A), I_{An} (A/m^2), I_{Cat} (A/m^2) and I_V (A/m^3) are current densities normalized by the anode surface area (A_{An}, m^2), cathode area (A_{cat}, m^2) and anodic chamber volume (V_R, m^3), respectively.

Power density is another widely used parameter to evaluate the power output of MFC. Power density is expressed as the power (P, W) provided by per unit surface area of electrode or volume of reactor. When the external resistance is equal to the internal resistance of an MFC, the maximum power density (P_{max}) can be achieved.

2.2 *NER*

Compared to the power output, energy output (E, J) in kWh is more appropriate to describe the energy generation of MFC in water and wastewater sectors.[18,19]

To convert energy from J to kWh, the following equation is used:

$$1\ kWh = 3.6 \times 10^6\ J \tag{4}$$

The energy recovery capacity from waste is expressed as *NER* in kWh/kg chemical oxygen demand (COD) or kWh/m^3 wastewater:

$$NER = \frac{E}{V_W} \tag{5}$$

$$NER = \frac{E}{\Delta COD} \tag{6}$$

where V_W (m^3) and $\varDelta COD$ (kg) are the volume of wastewater treated and COD removed respectively within certain reaction time span t_0 (s).

2.3 *CE* and *ECE*

CE is a parameter to evaluate the conversion from chemical energy to electrical charge. *CE* is defined as:

$$CE = \frac{\int_0^{t_0} I dt}{Fb\Delta M} \tag{7}$$

where b is the mole of electrons extracted from per mole of electron donor, ΔM the mole of electron donor reacted and F the Faraday constant (96485 C/e^-).

For complex wastes, it is more convenient to use COD as a measure of substrate concentration, and the *CE* thus becomes:

$$CE = \frac{8\int_0^{t_0} I dt}{FV_{An}\Delta COD} \tag{8}$$

where V_{An} is the volume of liquid in anode compartment and 8 is a constant calculated on the base of $M_{O2} = 32$ for the molecular weight of O_2 and $b = 4$ for the number of electrons exchanged per mole of O_2.

CE is related to electrical current, but a high current does not necessarily result in a great power output. Thus, *ECE* is proposed to represent the fraction of energy in a fuel cell that is captured as electricity:[20]

$$ECE = \frac{\int_0^{t_0} P dt}{e^-_{donor}(-\Delta G)} \tag{9}$$

where e^-_{donor} is the electron equivalents of electron donor, and ΔG the change in standard Gibbs free energy between the electron donor and electron acceptor (J/e^-).

So far, current density and power density have been extensively used in MFC-related studies. However, these two parameters reflect the power output of MFC only, but give no information about the correlation between energy production and waste removal. *NER* seems to be more appropriate to predict the energy performance of MFC with respect to waste treatment, because it provides energy information that is associated with the waste characteristics.[19] Nevertheless, power density is still essential for calculating the value of *NER*, and a higher power output generally results in a greater *NER*. *CE* and *ECE* are criteria directly related to the waste-to-electricity conversion. *CE* represents the amount of electrons delivered from wastes in the form of current, and *ECE* suggests the energetic efficiency that is dependent upon both voltage and current.[21] While *ECE* precisely describes the percentage of electric energy converted from wastes, it does not apply to wastes with unknown compositions, because it is hard to estimate their Gibbs free energy. In this case, *NER* can be used as an alternative to assess the energy recovery from wastes. Of course, multiple parameters should be comprehensively compared to get a thorough understanding of the energy performance of MFC, and both the power output and energy recovery efficiency should be taken into consideration in efforts to improve the energy-generating capacity of MFC.

3. Energy harvest from various wastes by MFC

Waste treatment is usually energy and cost intensive.[10,22] MFC is an emerging technology that promises direct production of electricity in waste treatment. Various chemicals ranging from small molecular organics to polymers can be used to fuel MFC, making it an ideal technology to extract energy from a variety of wastes.

3.1 Domestic wastewater

Modern water management is driving innovations in domestic wastewater treatment technologies with a focus on reducing energy demand and recovering energy, water and other resources. In conventional process of aerobic wastewater treatment combined with anaerobic sludge digestion, a large portion of the energy contained in dissolved organic fraction is not recovered but removed. In comparison, MFC allows a direct energy capture from dissolved organic component in the form of electricity with little offsetting energy expenditure. Especially, MFC has distinct advantages over anaerobic digestion in treating low-strength domestic wastewater.[23] The possibility of implementing energy self-sufficient MFC for domestic wastewater treatment has been envisaged based on the performance of liter-scale reactors.[17] In a 200-liter MFC stack (effective volume of 100 liter) fed with domestic wastewater, the highest power output of 114 mW was obtained, which is sufficient to drive a direct current (DC) pump (Fig. 2).[24] Another 250-liter stackable pilot-scale MFC produced a net power of 0.47 W/m^3, while the operation energy cost was only half of that in conventional aerobic treatment.[25]

3.2 Food wastes

Food processing wastes and food debris are attractive feedstock for bioenergy production because of the high moisture content, rich organic content and high carbon to nitrogen ratio that favor biodegradation.[26] Various food wastes, including canteen based food waste,[27] molasses wastewater,[28] starch processing wastewater,[29] brewery wastewater,[30,31] palm oil mill wastewater[32,33] and dairy wastewater,[34] have been tested as MFC fuels. Wastewaters containing high percentages of easily degradable carbohydrates, such as dairy wastewaters, brewery wastewaters and molasses, are usually more favorable for electricity generation than those rich in celluloses and lipids. An annular single-chamber MFC fed with dairy wastewater was reported to produce as high as 20.2 W/m^3 power density along with *CE* of 26.9%.[35] Food waste-fueled MFCs have a great potential for an energy self-sufficient operation in scaled up systems. A 100-liter stackable pilot-scale reactor fed with brewery wastewater in a continuous flow mode produced a total energy of 0.097 KWh/m^3, which could be used to power a pumping system (0.027 KWh/m^3) for self-sustained feeding (Fig. 3).[31]

Despite the high energy content of food wastes, their low ion conductivity is a constraint for MFC operation. Generally, power generation of MFCs can be facilitated by a high conductivity of up to 20 ms/cm,[2] whereas most food wastewaters have conductivities typically below 6 ms/cm.[36] Amendment of 100 mM NaCl to the food waste leachate enabled an increment of P_{max} from 366 to 1000 mW/m^3 because of the increased solution conductivity.[37] Food wastes rich in soluble COD sometimes need to be diluted to avoid microbial inhibition, for which low-strength wastewaters like domestic wastewater is preferred as a dilution medium.[38]

3.3 Landfill leachate

Landfill leachate generated from the disposal of municipal solid wastes contains a wide range of biodegradable organic matters, xenobiotic organic compounds, sulfide, ammonia and heavy metals. The abundance of organic carbon in landfill leachate makes it a desirable feedstock for MFC. However, the high COD loading and large amounts of poorly biodegradable organics and inhibitory compounds limit the energy production.[39,40] So far, power densities of the MFCs fed with landfill leachate were usually less than 1 W/m^3, and the *CEs* were lower than 20%.[41-48] In an upflow air-cathode membrane-free MFC, 12.8 W/m^3 electricity was produced from landfill leachate, but the *CE* was 1.2% only.[49] Excessively high COD concentration in landfill leachate can decrease the *CE*, even though it leads to an increased power output. In an MFC fed with young landfill leachate, increasing the COD loading from 1 to 50 g/L significantly decreased the *CE* from 57% to 1%.[46] Therefore, when landfill leachate is used to fuel MFCs, a proper dilution is strongly recommended to increase the *CE* and prevent the depression of power output by inadequate organic loading.

3.4 Complex industrial wastes

Recalcitrant compounds comprise a much greater proportion of the total carbon pool than the labile ones. A wide variety of recalcitrant chemicals, such as petroleum hydrocarbons,[50,51] chlorinated compounds,[52,53] nitrogenous compounds,[54] heterocyclic compounds[55-57] and polymers,[58,59] have been tested as MFC feedstock, but only a few studies used real-field wastes. MFCs exhibited high COD removal efficiencies for the treatment of paper recycling and pharmaceutical wastewater, whereas the power densities were lower than 1 mW/m^2.[60,61] In comparison, much higher power densities of 8 W/m^3 and 822.3 W/m^3 were obtained for dye wastewater and steroidal drug industrial effluent, respectively.[62,63]

The use of an electrode as an electron acceptor in soils or sediments is attractive, as the microbes responsible for degradation will co-localize with the contaminants at anode. Once in position the electrode can provide a continuous long-term electron sink for the biodegradation of harmful environmental contaminants. Microbial electrochemical remediation of petroleum-contaminated soil by an MFC has been demonstrated. Hydrocarbon degradation efficiency was improved from 2% in the open-circuit control to 24% in the MFC with P_{max} of 2162 mW/m^3.[64] The MFC constructed on a hexachlorobenzene-contaminated topsoil also showed a high pesticide removal efficiency of 71.2% with P_{max} of 77.5 mW/m^2.[65]

3.5 Sewage sludge

Sludge disposal expenses may account for up to 50% of the total cost for sewage treatment, and hence is a headache for many municipal wastewater treatment plants. Notably, a large amount of energy in wastewater enters into sludge after aerobic treatment process. Thus, sludge is a potential energy source to be exploited.[66] To date, the maximum power output of MFCs that use sewage sludge as fuel is 4.2 W/m^3 for an abiotic cathode system[67] and 13.2 W/m^3 for a biocathode one.[68] Sewage sludge is mostly present in the form of insoluble particulates, whereas microorganisms in MFCs prefer soluble and easily biodegradable organic matters. As a result, sludge pretreatments with ultrasonication, heating, alkalination or pre-fermentation are recommended to disintegrate the insoluble materials and thus enhance energy recovery efficiency.[69,70] Despite of the limited electricity generation, MFC is still an attractive technology for energy recovery from sewage sludge because CH_4 can be simultaneously produced in anodic chamber. A two-stage MFC system for sludge treatment achieved a total energy production (sum of electric energy and biogas energy) as high as 23.22 kWh/m^3 at a hydraulic retention time of 14 day, which is comparable with that in an anaerobic digester.[18]

3.6 Animal wastes

Modern livestock agriculture has drastically increased the production of animal wastes. Manure and urine contain abundant organic matters, and thus can be used as substrates for MFC. Reported power densities of animal waste-fueled MFCs were highly diverse, ranging from several hundred milliwatts to several watts per cubic meter reactor volume. The MFC powered by dairy manure obtained a P_{max} of

15.1 W/m^3 using biocathode,[71] and 16.3 W/m^3 in a cassette-electrode configuration.[72] However, in a 4-liter MFC of loop configuration fed with piggery wastewater, the P_{max} was 1.416 W/m^3 only.[73] The power density is affected by the solid and moisture contents in animal wastes. A continuous increase in the solid content from 2% to 10% led to an initial rise and subsequent sharp decrease in power density.[71] In another study, animal wastes with moisture contents of 80%, 70% and 60% achieved P_{max} of 349 ± 39, 36 ± 9 and 12 ± 2 mW·m^{-2}, respectively.[74] An unfavorable feature of animal wastes is the high concentration of ammonia, which severely inhibits the exoelectrogenic activity.[75] Nitrate and nitrite transformed from ammonia also reduce the energy recovery efficiency by competing with the electrode for electrons.[73,76]

3.7 Plant wastes

The abundance and renewability of lignocellulosic materials from plant wastes render them a promising feedstock for cost-effective energy production. The feasibility of MFC to use agricultural wastes, including corn stover,[77,78] wheat straw,[79,80] rice straw,[81] bean residue and ground coffee,[82] and aquatic plants such as the *Canna indica*,[83] as substrates has been evaluated. Lignocellulosic biomass contains abundant cellulose, hemicellulose and lignins, which cannot be directly utilized by exoelectrogens and have to be converted to monosaccharides or other low-molecular-weight compounds first. Therefore, hydrolysis and fermentation of lignocellulosic biomass are needed before it can be used for electricity generation.[84] The power output of MFC is generally restricted by the low biodegradability of lignocellulosic materials. As shown in Fig. 4, lignocellulosic materials contain polysaccharides in the form of cellulose and hemicelluloses, which are closely associated with lignin. It is difficult for microorganisms to access cellulose and hemicelluloses unless lignin is modified or removed. Thus, pretreatment aiming at breaking down the rigid structure of lignocellulose is necessary to improve their microbial accessibility.[85] Usually the pretreatment gives a carbohydrate-rich liquid hydrolysate by hydrolyzing cellulose and hemicelluloses.[77] By using *Oscillatoria annae* to converting the lignocellulose to glucose, a three-compartment MFC achieved very high P_{max} of 8.78 and 6.73 W/m^3, with sugarcane bagasse and corn cob as substrates, respectively.[86]

It is difficult to compare performances of MFCs in literature due to the different operational conditions, reactor configurations, types of electrodes and membranes and microorganisms involved. Yet, the potential of MFC to recover electric energy from real wastes can be approximately estimated. As shown in Table 1, the energy-generating capacities of MFCs vary significantly, depending on the composition, strength and solution chemistry of wastes. Differing from single substrate incubation, microbial degradation of complex substrates in real wastes features an energy-intensive process with intricate combination of sequential and parallel substrate degradation routes. As a result, simple wastes rich in biodegradable organics usually yield more energy than those containing complex substrates, refractory compounds or insoluble components.[20] Electron losses to competitive electron acceptors like nitrate, nitrite and sulfate can impair energy recovery from wastes. Compounds that inhibit the exoelectrogenic activity should be removed or converted because they can reduce the power output of MFC.

Acknowledging that many real wastes may not be suitable for directly fueling MFC from an energy production perspective, there are opportunities to lift the energy-generating capacity of waste-fed MFCs through improving the biodegradability of wastes and eliminating inhibitory and competitive compounds by pretreatment. Currently the average NER of MFCs fed with domestic wastewater is 0.04 kWh/m^3 wastewater or 0.17 kWh/kg COD, and industrial wastewater results in a value of 0.10 kWh/m^3 wastewater or 0.04 kWh/kg COD.[19] This NER level is quite low compared to the value of 0.34-0.49 kWh/m^3 wastewater or 0.69-0.98 kWh/kg COD obtained by conventional anaerobic digestion approach.[10] However, till date the highest NER observed in the MFCs is above 2.0 kWh/m^3 wastewater or 1.95 kWh/kg COD.[19] It is anticipated real waste-fed MFCs might achieve such an NER target after appropriate pretreatment to facilitate the waste degradation in MFCs. In addition to the energy recovery efficiency, power output of MFCs with real wastes also remains to be promoted. The power density of MFC should achieve 1 kW/m^3 to be competitive to anaerobic digestion[110], while most real waste-fueled MFCs have power densities below 10 W/m^3 (Table 1). Nevertheless, it is desirable to improve such power density to hundred watts via pretreatment, in the light of the highest power density of 200 W/m^3 obtained in a 4-liter MFC with acetate as the substrate.[111,112]

4. Factors constraining energy output of MFC

4.1 Thermodynamic limitation and energy losses

Progresses in reactor architecture, material and operation optimization of MFC have remarkably relieved physical and chemical constraints of MFC systems. However, the true power generation potential of MFC is still limited by the thermodynamic barrier and the high energy losses. Unlike chemical fuel cells, large power production cannot be easily achieved by simply connecting MFCs in series or parallel due to their nonlinear nature.[113-115] Up to now, the highest power density of a single liter-scale MFC is reported to be 200 W/m^3,[111,112] which is several orders of magnitude lower than those achieved by many other energy conversion technologies (Fig. 5a).[116] Even if the power of MFC is proportionally improved to the reactor volume, the maximum power output of a 1000 m^3 MFC will be no more than 0.2 MW, which is still insufficient to meet local power needs as a stationary power supply (Fig. 5b).

4.1.1 Thermodynamic limitations Thermodynamic limitations make MFC a low power system in comparison to other renewable energy systems such as solar and wind cells. MFC used to harvest energy usually employs O_2 as electron acceptor at cathode, which provides a standard cathode potential of + 0.805 V vs. Standard Hydrogen Electrode (SHE) under typical MFC operating conditions (T=293 K, pH=7, pO_2=0.2 bar).[17] At anode microorganisms consume substrate and produce intracellular reducing power stored in the electron carrier NADH. Thus, the anode should have a higher potential than the NADH to enable electron transport from microorganisms to electrode (Fig. 6).[117] Since the midpoint redox potential of NADH is -0.32 V vs.

SHE,[118] a voltage lower than 1.125 V across the two electrodes of MFC is expected regardless of substrates.

4.1.2 High energy loss inside MFC. In addition to the thermodynamic limitations, energy loss also arises from the various constraints inherent with the microbial device.[119] Microbial growth and metabolism at anode and activation of electrodes consume a large portion of energy. Direct electron flow from substrate to electrode is hindered by the transfer resistances, including anode and cathode resistances, electrolyte resistance, and membrane resistance. This minimizes the potential achieved from MFC and lowers the energy recovery efficiency. To reduce internal energy losses, a membrane-less microbial battery with Ag_2O/Ag cathode was recently adopted to recover 44% of the energy as electricity from glucose (Fig. 7).[120] But the energy recovery will be much lower when wastes are used as feedstock.

Electrochemical reactions at the electrode surface require activation energy for the electron transfer either from electron donor to anode or from cathode to electron acceptor. Energy losses at the anode of MFC are different from those for a chemical fuel cell, because the formation of anode-biofilm creates a unique environment. First, microbial metabolism involves energy loss. Microbes must capture energy from the potential difference between their electron donor and terminal electron carrier to support their growth and maintenance. Second, biofilm has its own ohmic resistance for electron conduction from microbial cells to anode surface, and mass transport within biofilm also consumes energy.[20] Both the intracellular and extracellular energy losses in substrate consumption and electron transfer within anode biofilm have been identified.[117] As shown in Fig. 6, two kinetic processes are involved in the intracellular energy losses from substrate to the outer-membrane proteins. At first, substrate oxidation produces intracellular reducing power, which takes the form of electron carriers like NADH. Then, the electron carrier is oxidized by transferring electrons to outer-membrane proteins. The relationship between the substrate utilization and the current generation fits the Monod equation (eq. 10), and the Nernst-Monod equation (eq. 11) could be used to describe the electron transport from reduced intracellular carrier to outer-membrane proteins:[121]

$$I = I_{\max}\frac{S}{K_{s,app} + S} \tag{10}$$

$$I = I_{\max}\frac{1}{1 + \exp[-\frac{F}{RT}(E_{OM} - E_{KA})]} \tag{11}$$

where I_{max} is the maximum current obtained by anode biofilm, S is the substrate concentration in liquid, $K_{s,\ app}$ is the apparent half-saturation substrate concentration in biofilm, R is the ideal gas constant, T is the temperature (K), E_{OM} is the potential of outer-membrane protein and E_{KA} is the potential at which I=1/2I_{max}.

The extracellular energy losses also involve two kinetic processes: one is the electron transport from outer-membrane proteins to anode surface through the conductive biofilm matrix; another is the electron transport from biofilm to anode electrode. The electron transfer within biofilm is restricted by the biofilm conductivity as described by Ohm's law (eq. 12), and the electron transfer at electrode interface is modeled by the Butler-Volmer equation (eq. 13):

$$I = -\frac{\kappa_{bio}(E_{OM} - E_{\mathrm{int}erface})}{\Delta z} \tag{12}$$

$$I = -I_0 \exp[\frac{nF(1-\alpha)(E_{anode} - E^0_{\mathrm{int}erface})}{RT}] \tag{13}$$

where κ_{bio} is the conductivity of biofilm, $E_{interface}$ is the potential at the biofilm-electrode interface, Δz is the electron transport distance within biofilm, I_0 is the exchange current, n is the number of electrons exchanged, α is the electron-transfer coefficient for the anodic reaction, E_{anode} is the anode potential and $E^0_{interface}$ is the standard potential of the reaction occurring at anode interface.

From Eqs. 10-13, the factors restricting current generation at anode (i.e., causing energy losses in electron transfer from substrate to anode electrode) could be identified. So far, most efforts in MFC improvement have focused on engineering better fuel cell architecture and/or materials with the implicit assumption that energy loss at anode biofilm is of negligible impact on the energy-generating capacity of MFC. In fact, there may be large opportunities to improve power production by overcoming the biological limitations.[122] A study on *Geobacter sulfurreducens* showed a direct correlation between biofilm conductivity and current density, clearly suggesting that the energy loss at anode biofilm is an important factor limiting the power output of MFC.[123] In particular, for the real-waste fueled MFCs the minimization of anodic losses is as important as minimization of cathodic losses, because of the interplay between the anode and cathode electrodes.[124] It should be noted that substrate losses to other electron sinks, such as methanogenesis, nitrate- and sulfate-reductions, H_2 scavenging and aerobic microbial growth, can significantly reduce the energy recovery efficiency of MFC in practical waste treatments.[125]

At cathode electrons are transferred to terminal electron acceptor. This process is currently recognized as the bottleneck confining the energy output of MFC (Fig. 8).[126] In analogue to other chemical and biological fuel cells, the cathode activation loss is mainly due to the high energy barrier for O_2 reduction.[127] The O_2 electro-reduction is a complex process involving several electrons and many possible pathways. In the past decades great efforts have been made to improve catalyst efficiency and reaction kinetics, whereas the overpotential for cathodic O_2 reduction is still substantial. Particularly, the activation energy for O_2 reduction is positively correlated to the electrode potential according to the ab-initio molecular dynamics based on a four-step pathway (eqs. 14-17, Pt atom is used to coordinate with O_2, $HO_2\cdot$, H_2O_2 and $HO\cdot$) (Fig. 9A).[128]

$$Pt-O_2+H^+ + e^- \rightarrow Pt-OOH \tag{14}$$

$$Pt-OOH+H^+ + e^- \rightarrow Pt-OHOH \tag{15}$$

$$Pt-OHOH+H^+ + e^- \rightarrow Pt-OH+H_2O \tag{16}$$

$$Pt-OH+H^+ + e^- \rightarrow Pt-OH_2 \tag{17}$$

Similar results are obtained from density functional theory calculations for O_2 reduction following another reaction cycle on the Pt (111) surface (eq. 18-21). The energy barrier increases monotonically with the increasing electrode potential (Fig. 9B).[129]

$$H^+ + e^- \rightarrow Pt-H \tag{18}$$

$$O_{2_{gas}} \rightarrow Pt-O_2 \rightarrow 2Pt-O \qquad (19)$$

$$Pt-O+(H^+ + e^-)/Pt-H \rightarrow Pt-OH \qquad (20)$$

$$Pt-OH+(H^+ + e^-)/Pt-H \rightarrow Pt-OH_2 \qquad (21)$$

Therefore, in the presence or absence of catalyst, more activation energy is required to obtain a high cathode potential. Even worse, many chemical catalysts suffer from much poorer catalytic performance in MFC than in chemical fuel cells due to the suboptimal operational conditions, resulting in more energy lost at cathode.[130] In addition, mass transport limitation in the cathode compartment is typically more severe than that in the anode compartment because of the low solubility of O_2 in water.[131] For biocathode, bacterial growth and mass transfer within biofilm also contribute to the energy losses.

The separating membrane between anode and cathode assures a high selectivity for protons and environmental stability for bacteria growth, but it also causes substantial energy loss. Membrane resistance originating from the low accessibility of liquid electrolytes onto membrane surface is identified as the primary internal resistance of MFC. In electricity generation processes, electron transfer through circuit is accompanied by ion diffusion across membrane to maintain electroneutrality. Insufficient ion transport through the membrane not only causes increment in membrane resistance, but also leads to pH-splitting problem, i.e., acidification of the anodic side and alkalization of the cathodic side.[132,133] In general, anion exchange membrane suffers from less energy loss caused by pH-gradient than cation exchange membrane, but is more prone to substrate permeability and deformation.[134,135] Compared with ion exchange membranes, size-selective separators, like microporous filtration membranes, porous fabrics, glass fiber and nylon mesh, usually show higher ion transport ability and lower internal resistance.[93,134,136-138] However, the *CE* is concomitantly reduced as a result of the increased substrate and O_2 permeations through the separator pores. While the development of MFC separator seems to be confronted with a dilemma between charge transfer and mass permeation,[139] several emerging approaches show a potential to alleviate such a problem. Proton conductance across ion exchange membrane can be facilitated by introducing hydrophilic material into membrane structure, thus raising both the power output and *CE* of MFC.[140, 141] Separator electrode assembly configuration with porous separator and electrode bound together is found to prevent substrate and O_2 permeations through porous separator, leading to an increased *CE*.[142,143] Osmotic MFCs with forward osmosis membrane exhibit promising electricity generation by making use of water flux to accelerate ion transport and keep O_2 out of anode.[144,145] Forcing electrolyte to flow continuously from the anode chamber to the cathode chamber is also effective to promote proton flow while limit O_2 diffusion in two-chamber MFC.[146] At the present stage, the poor separator performance is still one major barrier limiting the energy output from MFC, and there is much to be done to reduce the separator-induced energy loss.

Electrolyte resistance coming from ionic flow through the electrolyte determines the energy loss associated with mass and charge transport in solution. Such an energy loss can be reduced by increasing solution conductivity, while the susceptibility of bacteria to the added electrolytes should be taken into consideration. In comparison, reducing the electrode spacing can decrease the mass diffusion distance and is a more feasible option to reduce the electrolyte resistance. [111,147,148]

4.2 Instability of power output

Stable power output is an essential requirement for an electricity generator. However, the poor longevity of MFC severely restricts its potential as a direct power supplier. As shown in Fig. 10, MFCs after long-term operation, especially those fueled with real wastes, inevitably suffer from performance deterioration with violent fluctuations in the power output.[149] To date, some attempts have been made to resolve this problem, but truly effective and practical countermeasures are still lacking.

4.2.1 Performance deterioration of MFC. The main internal deteriorations responsible for the MFC performance decline are summarized in Fig. 11. The exoelectrogen biofilm, which varies depending on the microbial growth and decay, is an important factor governing the energy conversion in MFCs. According to the electron transfer from anodic microbes that are not in intimate contact with the electrode,[150,151] improving availability of effective biocatalysts would enhance the MFC performance until mass transfer within a thick and dense biofilm becomes limiting.[152] Excessive bacterial colonization on anode over time brings about high resistance to the substrate diffusion and charge transfer.[153,154] In addition, anode materials with multifarious porous structure favor the internal colonization of microorganisms.[147,155-162] However, macro- and micro-pores with diameters normally less than 10 μm are easily clogged by microbial growth. In this case, the non-conductive cellular debris after cell death inclines to accumulate in pores and prevent mass and electron transfers because of inaccessibility of inner anode surface to the active exoelectrogens.[21,163] Compared to the severe deteriorations of cathode and membrane, anode biofilm decay may have less influence on the long-term performance of MFC.[126] Nevertheless, it should be noticed that in practical waste treatment severe performance deterioration of MFC may occur as a result of irreversible damage of biofilm due to a drastic environmental variation or harsh hydrodynamic force.

The O_2 reduction reaction catalyzed by chemical catalysts (usually Pt) is the most dominant cathodic reaction in MFC. The unlimited availability and high standard redox potential of O_2 in air make it an ideal electron acceptor, but chemical catalysts for O_2 reduction suffer from performance decay during long-term operation. Power output was found to drop by 21% when a biofilm was formed on the Pt-catalyzed carbon cloth cathode, and removal of the cathode biofilm completely restored the power output to its original level (Fig. 12A).[164] Here, the formation of cathode biofilm blocked the proton transfer to the catalysts.[165,166] However, in addition to biofilm, other factors can also cause cathode deterioration. Pores in cathode could be clogged over time, resulting in raised O_2 diffusion resistance.[167] Owing to the accumulation of alkali salt and low air humidity at the cathode side, a 10-liter MFC stack treating brewery wastewater exhibited a 60% decrease in P_{max} during the incubation period from 30 to 180 days (Fig. 12B).[92] Biocathodes seem to be more stable than chemical ones in the over 400-day operation of MFCs.[168] However, in practical waste treatment biocathode may suffer from more severe deterioration because of microbial susceptibility.

The inevitable membrane fouling during long-term operation of MFC can significantly deteriorate its power generation performance. Accumulation of high-valent ions in membrane pores would block ion transport channels and raise electrical resistance. It was found that, after 400-day operation, the power density of a two-chamber MFC dropped by 26.6% due to the hindrance of ion transport by cations inside the membrane.[169] Biofouling due to the formation of biofilm on membrane surface can significantly deteriorate the membrane performance. The fouling layer, which consisted of microorganisms encased in extracellular polymers and inorganic salt precipitations, was found to lower the ion exchange capacity, conductivity and cation diffusion coefficient of proton exchange membrane (Fig. 13). As a result, the internal resistance of MFC was remarkably increased by 20% and the open circuit voltage was reduced by 9.9%, leading to a 32.3% decline in P_{max}.[170]

4.2.2 Fluctuation of power output. MFC is highly sensitive to environmental upset. Variations of parameters such as pH, temperature and organic loading rate can substantially affect the microbial metabolism and the energy output of MFC. Generally, bacterial growth requires pH close to neutral, and pH change not only alters substrate metabolic activity but also affects the electron and proton generations.[171-174] The power density of MFC fed with domestic wastewater was found to vary from 0.36 to 0.66 W m^{-3} in a pH range of 6.0-9.5.[175] Temperature also influences the MFC performance. A moderately higher temperature favors power generation because of more active microbial metabolism, improved membrane permeability and solution conductivity.[176-178] Raising the temperature from 20 to 40 °C was found to increase the P_{max} of MFC by 38%.[179] Since the power output of MFC depends upon the substrate conversion rate, organic loading rate affects the MFC performance. Increment in power output was noticed as the organic loading rate was increased, but a too high organic loading rate would reduce the power density and *CE*.[27,180-182] In general, steady operational condition should be maintained to favor a stable power output of MFC. Unfortunately, operating condition control is usually difficult in practical waste treatment, which could lead to unpredictable fluctuation in the power output of MFC. In a study on sewage sludge-fueled MFC, a drastic fluctuation of current density from zero to the maximum value was observed due to the large variation in chemical content of feeding sludge.[18] Inevitable fluctuation of power output impairs the power quality and system reliability of MFC, making it difficult to balance the power supply and demand.

The use of real wastes as fuel and mixed microorganisms as catalyst brings about inherent constraints to the energy conversion in MFCs. Although higher electricity-generating ability of exoelectrogens may be expected in the future, currently the power output of individual MFC is still too low to compete with other energy conversion devices. In addition, the unavoidable performance deterioration over time and power fluctuation of MFC increase the difficulty in achieving reliable power supply. In the light of experiences from other renewable sources like wind and marine current energy, introduction of an energy storage device into circuit is assumed to be a good solution to boost the power output, mitigate the power fluctuation and improve the power quality of MFC.[183,184]

5. Energy capture and store with MFC

At present the direct power output of MFC or MFC stacks is not sufficient and stable enough to support continuous operation of any commonly used electric appliance. Thus, how to virtually utilize the MFC energy for real-world application remains one main challenge. To harvest usable MFC energy, it is necessary to integrate devices that can capture and store energy and boost the power output of MFC. Power converter-based energy storage device has been recently explored to replace external resistor that is utilized to show the power output of MFC.[185] The electronic circuit can operate as an equivalent external resistor, but energy generated from MFC can be harvested in storage instead of being dissipated as heat.[186-188]

5.1 Energy storage technologies for MFC

At present the electrochemical capacitor is predominantly applied to deposit MFC energy for driving low power-consumption instruments.[24,31,188-193] An electrochemical capacitor is a typical energy storage device composed of two conductive terminals separated by a dielectric material. The charge-storage of capacitor is completed predominately by utilizing a double-layer charging effect, but pseudo-capacitance also partially contributes to this process. Now capacitors capable of quickly absorbing or liberating a high amount of energy during hundreds of thousands of cycles without the release of heat and hazardous substances have been developed. The main advantage of a capacitor lies in its efficacy to smooth high-frequency power fluctuations, thus improving power quality.[184]

Through alternate charging and discharging, the outputs of current, voltage and power from MFC can be multiplied. Since capacitor stops charging when the voltage reaches the open circuit voltage value, MFC stacks and multiple capacitors are used to boost the power output. By charging an array of parallel-connected capacitors from four MFCs and then discharging them in series, the output voltage was found to increase from 0.7 to 2.5 V, meanwhile peak power was improved by 2.6 times with negligible energy loss in circuit.[194] When a capacitor was integrated with an MFC anode by using a capacitive electrode, exoelectrogens growing on the capacitive electrode can directly transfer the produced electrons to the electrode for storage.[195-197] Such an electrode design is able to improve the power output of MFC, while the energy storage capacity remains to be improved in comparison to an external capacitor.

Superconducting magnetic energy storage system stores energy in the magnetic field created by a flow of direct current in a superconducting coil (inductor). It is the only known technology to store electrical energy as current circulating through a coil that is made from a superconducting material and circular indefinitely. Once the superconducting coil is charged, the current will not decay and the magnetic energy can be stored. The magnetic energy storage system can harvest 67% energy from

MFC.[198] Although the implementation of magnetic energy storage device is costly, the minimal amount of energy loss and high quality of power output make it an attractive option for the MFC energy storage.[199]

5.2 Capacitor-based power management system

The use of a capacitor cannot produce a continuous power output, but it does allow an intermittently supply of higher power. This is acceptable, especially for some environmental monitoring sensors that are operated in an intermittent mode. In such a case, capacitor is usually used together with a charge pump, a boost converter and load, constituting a power management system (Fig. 14). The charge pump draws a low current from the MFC to charge the capacitor, while the boost converter is used to lift the output voltage of the capacitor to the voltage level of load.[200] The power management system has been proven useful to assist the benthic MFCs as a long-term power source for remote sensors.[189-192]

Another application pattern of the circuitry is the self-sustainable MFC stack. An MFC stack made from 40 identical 20 mL units of single-chamber 3D-printed MFCs was developed to perform its daily regime of feeding, hydration, self-sensing and reporting by using its own power.[188] Electricity generated from this MFC stack was used to continuously run a microcontroller for self monitoring and reporting the stacks' voltage and environmental temperature every 10 min. It was also used to simultaneously charge a 12.5-F supercapacitor pack to power the stacks' anolyte feeding at 48-hour interval and catholyte hydration at 12-hour interval. When the MFC stacks are scaled up their power output is able to run electric devices such as DC pumps. The power of an MFC stack composed of 24 tubular MFCs with 2-liter working volume was charged into the 25-F ultracapacitors through a battery management evaluation module (EVM) board (Fig. 2).[24] The output voltage of ultracapacitors was stabilized at 3.5 to 4.5 V to power the DC pump while input voltage was only 1 V. Self-powered active-feeding pattern has been demonstrated by a 100-liter brewery wastewater-fed MFC stack with five capacitor-based circuits charged in parallel and discharged in series (Fig. 3).[31] Notably, the energy consumption for pumping was less than half of the total energy produced by the MFC, thus enabling extended functionality with excess energy. Recently, a 6-liter MFC was constructed which harvested 0.27 kWh/m^3 energy from synthetic wastewater with COD of 1000 mg/L. By using a circuit made up of 3.3-F capacitors and relays controlled by programmable microcontroller, the generated energy was used to power both the pumping system for MFC (at energy consumption of 0.014 kWh/m^3) and another intermittent aeration system for biological filter (at energy consumption of 0.22 kWh/m^3).[201] By virtue of a power management system, more durable power is conceivable from large-scale MFC stacks to drive electric appliances in waste treatment plants.

To date almost all reported power management systems for MFC energy harvest have been focused on DC output to power small electronic devices. However, general electrical appliances in waste treatment require alternating current (AC) power to operate, which raises the need to develop energy management system that is able to conduct DC-AC power conversion for large-scale MFCs. A DC-AC converter that can generate alternating voltage in any desired frequency at ≥95% efficiency was recently developed.[202] However, how to incorporate such a converter with a capacitor remains a challenge.

The circuit with a resistor connected between anode and cathode indicates the amount of power that can be continuously supplied by an MFC, but it does not capture any usable energy. When an MFC is connected with a capacitor as an energy storage device, traditional evaluation criterions based on the circuit with an external resistor becomes not suitable. Alternatively, the circuit should be evaluated in term of energy harvested by a capacitor.[203] Specifically, information on the capacitor value, the charging potential allowing maximum energy harvest and the charging frequency achieving a desired charging potential will be important for the system performance evaluation.

Now the study about power management system for MFC is in its infancy. There are a variety of electrical energy storage technologies, including capacitor energy storage, superconducting magnetic energy storage, battery energy storage, flywheel energy storage, pumped hydro energy storage and compressed air energy storage, available for energy systems at different power scales. Capacitor is the most suitable candidate for energy storage with a consideration of the present power level of MFC, yet its performance as a long-term energy storage device for large-scale MFCs is still to be evaluated. Other energy storage technologies should also be tried to adapt to the development of MFC and to fulfill diverse application demands.

6. In-situ utilization of energy generated in MFC

Since the power output of individual MFC cannot continuously drive common electronics, in-situ utilization of the electrical energy generated from MFC has to be considered. There have been several systems developed so far using the MFC platform with different functions or system constructions (Fig. 15).

6.1 Microbial electrolysis cell (MEC)

MFC can be operated in a “microbial electrolysis cell” (MEC) mode, in which power originated from anode is invested to drive thermodynamically unfavorable reactions at cathode. A typical application is the use of an external voltage higher than 0.25 V on top of the MFC potential to initiate H_2 evolution at cathode through reduction of protons.[204,205] Such a voltage is much lower than that used in traditional water electrolysis (1.8-2.0 V). Notably, an MFC can be connected with an MEC to satisfy extra power demand. In an MEC-MFC-coupled system, bioenergies from the anodes of MFC and MEC were integrated to overcome the thermodynamic barrier from protons to H_2, thus realizing H_2 harvest from wastes.[114,206]

Similar strategies can be used to produce other chemicals in cathode chamber. Fig. 16 illustrates the external voltages applied to trigger the synthesis of various chemicals at cathode reported in literature. The production of CH_4 and organic acids such as formic acid and acetate was achieved in a process, which utilized the electrons from anode to reduce CO_2.[207-209] The feasibility of producing cathodic hydrogen peroxide (H_2O_2) through two-electron pathway of O_2 reduction combined with the microbial oxidation of organics at anode was also demonstrated.[210] Under an external voltage of 0.5 V, this system was capable of producing H_2O_2 from acetate at an efficiency of 83%. Since H_2O_2 generated at cathode is apt to self-decompose in water, it is proposed to be in-situ utilized to degrade biorefractory pollutants under the catalysis of ferrous iron.[211] The energy of MFC can also be utilized for the metal recovery from waste streams. Metals with high reduction potentials are directly recovered at cathode and those with low reduction potentials are recovered in the aid of an external power supply. To recover Cu, Pb, Cd and Zn from wastewater, external voltages of 0, 0.34, 0.51 and 1.7 V were required, with corresponding energy consumptions of 0, 3.8, 7.7 and 283.9 kWh/kg metal, respectively.[212]

6.2 Microbial desalination cell (MDC)

The concept of MDC is established by making use of the chemical energy stored in organic matter to create a potential gradient across anode and cathode to drive desalination.[213] A typical MDC unit consists of an anode chamber responsible for organic degradation and electricity production, a middle chamber for ion separation and a cathode chamber for completing the electric loop (Fig. 15). In contrast to other water desalination techniques that require power input, the MDC technology is advantageous for extracting pure water from seawater and meanwhile gaining net energy from wastewaters. For example, a liter-scale upflow MDC produced an energy of 1.8 kWh, accompanied by reducing 90% of salinity from 1 m^3 of seawater. In comparison, the recovery of 50% water in reverse osmosis system consumed 2.2 kWh energy.[214]

6.3 MFC-assisted photoelectrocatalytic (MPEC) system and bio-photo electrochemical cell (BPEC)

Photocatalytic oxidation is a promising process for degrading organic pollutants, but it suffers from recombination of photogenerated electrons and holes, which severely depresses the photocatalytic efficiency. This problem was resolved by connecting a photocatalytic system with an MFC to supply external anodic bias.[215] Notably, pollutant degradation rate in this integrated system was two times the sum of the rates by individual photocatalytic and electrochemical methods, indicating that the MFC and photocatalytic system were enhanced by each other.

Bioelectricity generated at anode can also be used to assist H_2 evolution at a photocathode. A self-bias BPEC with MoS_3-modified silicon nanowire photocathode was constructed to realize spontaneous H_2 production and electricity generation under visible light illumination.[216] In such a system, photogenerated holes in the valence band of semiconductor cathode were trapped by electrons coming from the bioanode, while the photo-excited electrons were combined with protons to form H_2. In this way, recombination of the electrons and holes generated under illumination were effectively retarded, resulting in favorable H_2 production.

The functions of MFC have been extensively expanded in above systems, which share microbial oxidation reaction at anode whereas harness electron flow to satisfy various purposes. The advantage of these systems is that the electrical energy generated at anode is in-situ utilized with a minimum energy loss. However, it should be noted that such an in-situ utilization strategy requires an integration of MFC with other energy-consuming processes, which may introduce additional impacts on the anode and cathode reactions. For example, electron flow in the MPEC is different from that in a single MFC. In addition to protons, the cations and anions also migrate in the MDC. In an MEC system, some aggressive cathode products such as H_2O_2 and H_2 are generated, which may lead to the deactivation of chemical catalysts. Therefore, energy generation and consumption inside the system should be appropriately coordinated to maximum the synergies.

7. Challenges and perspectives

In the context of wastewater treatment, it has long been hypothesized that MFC offers the advantage of energy self-sufficiency, instead of energy consuming.[217] The main energy consumers in MFC operation are pumps for feeding, mixing and recirculation. According to the state-of-the-art practice in domestic wastewater treatment, an MFC consumes about 0.024 kWh/m^3 wastewater for reactor feeding and mixing, but produces 0.026 kWh/m^3 wastewater of electricity.[149] For food wastes, to sustain the pump system of a brewery wastewater-fueled MFC, a total energy of 0.027 kWh/m^3 wastewater was required, which was only 27.8% of the total energy produced.[31] Therefore, a net-positive energy balance in practical waste treatment is conceivable if the energy potential in waste could be better exploited by MFC. This requires effective measures to reduce energy loss inside MFC, suitable pretreatment to liberate biodegradable substrates from waste, and integration of energy management system to boost and stabilize power generation from MFC.

The potential energy stored in different wastewaters ranges from 4.92 to 7.97 kWh/kg COD,[218] but currently MFCs recover less than 1.0 kWh/kg COD energy in real wastewasters.[19] Thus, there is room for MFC to improve energy recovery from wastes. In order to lessen energy loss to the anode biofilm, genetic engineering is highly recommended to construct exoelectrogen strains with superior electron conductivity;[219] the optimal biofilm thickness to allow efficient electron transfer and substrate access should be pursued; novel electrode design, such as 3D macroporous electrode, is needed to provide scaffold for microbial colonization while avoid cell clogging.[163] In addition, O_2 reduction efficiency at cathode is expected to be promoted by developing novel alloy or biomimetic catalysts of high activity, selectivity, and durability under the operating conditions of MFC.[220,221] Development of composite membrane and forward osmosis membrane is encouraged with a high ionic conductivity, low mass permeability, and less susceptibility to biological and chemical foulings.[140,141,144,145] At present, the estimated cost of an MFC system is 800 times higher than that of an anaerobic system, attributed mainly to the high costs of electrode and separator materials.[222] In the future development of electrodes and separators, low-cost materials should be pursued to reduce the economic barrier of MFC in waste treatment facilities.

Acknowledging that the power output of MFC is too low to directly drive commonly used electronics at the present time, tremendous efforts have been devoted to advancing the reactor assembly, material, and operation of MFC. However, in practical waste treatments the chemical composition of feedstock has even more important influence on the MFC performance than the reactor itself. Complex substrates in real wastes usually result in lower electricity generation than simple ones because of more complicated degradation pathways and hence more energy losses.[17] Also, the frequent presence of competitive electron acceptors in wastes further lowers the energy recovery efficiency of MFC. Therefore, in the design and operation of MFC, priority should be given to the conversion of carbon-diverse wastes to substrates favored by exoelectrogens and the mitigation of electron losses due to undesirable electron acceptors. This would need a multi-stage approach. It has been well established that running MFC systems in series or implementing anaerobic pretreatment can increase microbial accessibility to practical wastes and lower the competitiveness of other electron acceptors like nitrate.[41,47,223] For some wastes rich in biorefractory components, the pretreatments with costly chemicals or physiochemical methods are necessary to enhance the biodegradability of wastes, but energy content of wastes is simultaneously reduced in the pretreatment. Hence, pretreatment should be carefully controlled to supply biofavorable substrates at a minimum energy expense and economic cost. For example, a 3.6-liter two-stage MFC system fed by untreated primary sludge at a hydraulic retention time of 14 day produced total energy of 23.22 kWh/m^3 anode liquid volume over 120-day operation. Thus, the NER was approximately 2.71 kWh/m^3 sludge, which is equal to 0.05-0.11 kWh/total suspended solids (TSS) based on the TSS of sludge varying from 23.8 to 58.4 g/L.[18] Yet, the energy consumption of ultrasonic, ozone and thermal (at 90 °C) pretreatments for solubilizing sewage sludge could be as high as 2.60-2.80, 4.49-5.13 and 40.32-45.52 kWh/kg TSS, respectively.[224] While various pretreatment methods have been used in MFC studies, the economic issue is given little attention. To select and optimize pretreatment methods for MFC, it is time to perform comprehensive evaluation on the operation expenses of pretreatment, the costs associated with energy loss in pretreatment, and the revenue benefits from the enhanced biodegradability of wastes.

Despite the potential of MFC in generating electricity from real wastes, how to take advantage of the MFC energy is a key challenge. It should be admitted currently the energy capacity of individual MFC is not sufficiently high to support continuous operation of electric appliance. Even though the power output can be somewhat improved by using MFC stacks, the performance deterioration and fluctuation occurring during long-term operation remain a significant barrier limiting its application. Therefore, effective energy management systems are urgently required to lift power quality from MFC. Although many commercial energy management systems are already available, systems tailored for MFC is to be developed yet. Specifically, energy management system capable of generating AC power should be pursued to favor the use of MFC energy for a wide range of electrical appliances. Supercapacitor is anticipated to be a lucrative candidate for the MFC energy storage due to its high energy capacity, flexible design and excellent ability to stabilize the power supply. Capacity-based energy management systems have been reported by several groups, yet the charging and discharging processes are not well controlled. Charging and discharging potential and frequency as well as capacitor value are selected manually by trial and error within the operable range, which makes it difficult to fully extract energy from MFC. Regulation of charging and discharging processes adaptable to MFC power output is a primary task to ensure reliable energy storage and liberation.

Scaling up MFC to a practical level is essential to its technological and economic viability. However, even at field-scale MFC cannot meet the power generation requirements as an independent electric energy supply. Nevertheless, it may be integrated into a hybrid energy system and be used as a supplement to the conventional power generation facilities. A hybrid energy system usually combines renewable and conventional energy sources to reduce economic and environmental costs of fuel-based power supplies.[225] Hybrid systems based on wind or solar energy bear a good potential in the real-world applications,[226,227] which inspires us that the projecting of MFC-based hybrid energy systems might be a feasible way for the field-scale MFC. The concept of hybrid energy system is also promising to provide more reliable power from small-scale MFCs for some low power-consumption niches. A multi-source system that manages energies from MFC and acoustic piezoelectric harvester has been designed to meet the demand of perpetual energy supply for underwater wireless sensor networks.[228] In another study, a hybrid dielectric elastomer generator-MFC energy harvester was applied to EcoBot.[229] The EcoBot operation was characterized by dormant periods for energy storage from MFC, followed by the activation of the EcoBot using stored energy. Also, dielectric elastomer generator, driven by wind or water, was used as an alternate energy harvester to prolong active periods of EcoBot. The MFC-based hybrid energy system could be a new frontier in MFC research to put this technology into practice. Since the operating characteristic is distinct for each energy resource, MFC and other energy resources should be compatible in a hybrid system. Energy management systems with functions of energy storage, control and distribution need to be integrated with the hybrid system to assure the quality and reliability of energy output.

Although the level of MFC power output can be lifted by using an energy storage device, energy loss inevitably occurs in each charging and discharging process. In comparison, the in-situ utilization strategy enables the electric energy generated from MFC to be directly and more efficiently exploited. The experience at our laboratory on MEC, MPCE and BPEC studies demonstrates that there are numerous possibilities to harness electron flow from MFC to facilitate reduction-based processes. Particularly, MEC-based microbial electrosynthesis represents a great opportunity for chemical production. The microbial electrosynthesis in its nature allows on site transformation of wastes at anode to expected products at cathode via electricity. One notable merit of MEC is that the drawback derived from unstable energy output of anode can be compensated by adjusting the intensity of an external power supply. To forward this technology efforts are needed to seek for high product specificity. Therefore, bio-catalyzed electrochemical reactions occurring in MFC provide inherent advantages to utilize chemical energy in real wastes for diverse applications. Strategies for in-situ utilization of the MFC power should be explored when extending the application scope of MFC, and integration of MFC with other technologies at low-energy demand should be encouraged.

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Table 1 Power output from liter-scale MFCs fueled with various real wastes

Type of waste	Reactor configuration	Reactor volume (L)	Maximum power density		Maximum *CE* (based on COD)	Ref.
			Normalized by anode volume (W/m^3)	Normalized by anode area (W/m^2)		
Urban wastewater	Two-chamber MFC	1		0.025		87
Domestic wastewater	Membrane electrode assembly MFC	3.5	2		0.9	88
Domestic wastewater	Multi-anode/cathode MFC	20		1.500		89
Domestic wastewater	MFC stacks (parallel connected)	1.872 (156 mL per unit)	248		77.8	90
	MFC stacks (series connected)		228		12.4	
Palm oil mill effluent	Upflow membrane-less MFC	2.36		0.0446		32
Ultrasonically pretreated palm oil mill effluent	Two-chamber MFC	4	18.33	18.96		91
Brewery wastewater	Serpentine-type MFC stack	10 (250 mL per unit)	6.0		7.6	92
Brewery wastewater	Baffled MFC	100		0.181	19.1	31
Sugar refinery wastewater	Single-chamber MFC	1	1.495		5.37	93
Protein food industry wastewater	Two-chamber MFC	1.5		0.2303	15	94

Cassava mill wastewater	Single-chamber MFC	30		1.800	20	95
Acidogenic food waste leachate	Two-chamber MFC	3	15.14		66.4	96
Landfill leachate	Single-chamber MFC	1		0.0018		41
Landfill leachate	Two-chamber MFC	1		0.00135		42
Landfill leachate	Single-chamber circle MFC	1.89		insignificant	5.2	48
		1	0.844		41%	
Landfill leachate	Membrane-less MFC	3.5	2.71			97
Sewage sludge	Two-chamber MFC	1	45.34	0.04534		98
Sewage sludge	Membrane-less	1	2	0.29		99
Primary sludge	Tubular MFC	1.8	6.4		7.2	18
Digested sludge			3.2		2.6	
Primary sludge	Two tubular MFCs (series connected)	1.8	8.5 (MFC1) 10.7 (MFC2)		2(MFC1) 4(MFC2)	
Thermo-chemical pretreated dairy waste activated sludge	Two-chamber MFC	1.35	0.715		9	100
Animal carcass wastewater	Up-flow tubular air-cathode MFC	1.2	2.19		0.25	101
Swine wastewater	MFC stacks (parallel connected)	1.475 (295 mL per unit)		175.7	0.1	102
Cattle manure solid waste	Twin –compartment MFC	1.8	0.3	0.093		103
Cattle dung	Two-chamber MFC	15	0.22		2.79	104
Piggery wastewater	Loop configuration MFC	5	0.0014			73
Chemical wastewater	Two-chamber MFC	1.5	2.02			105
Mixture of domestic wastewater and real textile wastewater	Membrane-less cross-linked MFCs	4 (2 L per unit)	750		36	106
Bermudagrass straw	Two-chamber MFC	2		0.00000309		107

Avena L. straw	Soil MFC	0.0108	108
Acorus calamus leaves	Sediment MFC	0.195	109
Wheat straw		0.167	

Figure captions

Fig. 1 Electricity generation from wastes by MFC.

Fig. 2 A) Prototype of a 200-liter MFC stack fed with domestic wastewater; B) Schematic of charging/discharging circuit connection; and C) Charging and discharging of the ultracapacitors to drive a DC motor. When the voltage of the ultracapacitors reaches 4.5 V, they are discharged by powering the motor. When the voltage is lower than 3.5 V, unltracapacitors are disconnected from the motor and charged by the MFC stack until the voltage is 4.5 V (adapted with permission from ref. 24. Copyright 2015 Elsevier Ltd.)

Fig. 3 A) Schematic diagram; B) Photo of the 90-liter stackable baffled MFC fed with brewery wastewater; C) Electrical energy allocation controlled by a float switch. When the liquid level in the head tank falls 1 mm below the height at which the switch is installed, the capacitors are discharged through the pump. When the liquid level rises to the height at which the switch is installed, the energy is harvested by the 5 Ω resistor; and D) Changes of operating voltage across pump and resistance. The maximum voltage on the pump is 4.2 V, which is sufficient to meet the energy requirement for pumping (adapted with permission from ref. 31. Copyright 2015 Elsevier Ltd.)

Fig. 4 Enhancement of pretreatment on exoelectrogenic accessibility to lignocellulosic materials.

Fig. 5 Comparison of: A) power density; and B) power level between MFC and other energy conversion devices in transportation propulsion and stationary power sectors (data are obtained from refs. 111, 112 and 116).

Fig. 6 Schematic of the electron transfer process at anode of MFC with sequential energy losses.

Fig. 7 Energy recovery in a glucose-fed microbial battery with an Ag_2O/Ag solid-state cathode (adapted with permission from ref. 120. Copyright 2013 PNAS).

Fig. 8 A) Nyquist plots showing a significant contribution of cathode impedance to the total impedance of MFC; and B) Behaviors of anode, cathode and solution membrane impedance over time during the enrichment of exoelectrogens in the MFC (reprinted with permission from ref. 126. Copyright 2010 American Chemical Society).

Fig. 9 A) Activation energy for the four steps of O_2 reduction as a function of electrode potential. Heavy lines connect points with species undergoing reduction bonded to a platinum atom. Dotted lines connect points with no bonding to the platinum. The same key applies to both sets of curves; and B) Energy barriers for the O_2 reduction calculated by density functional theory (Reprinted with permission from refs. 128 and 129. Copyright 2000 The Electrochemical Society, Inc. and 2012 American Chemical Society).

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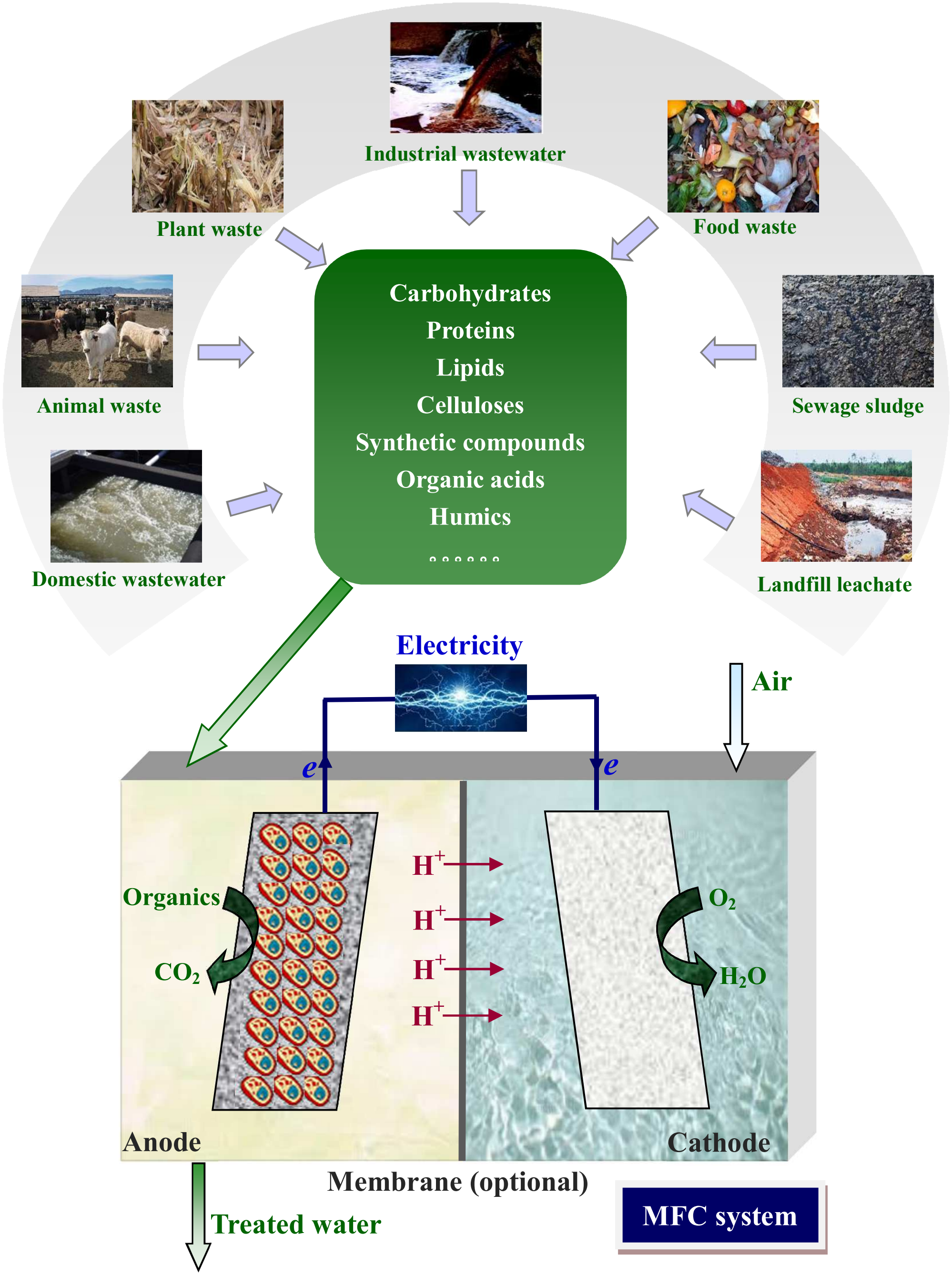

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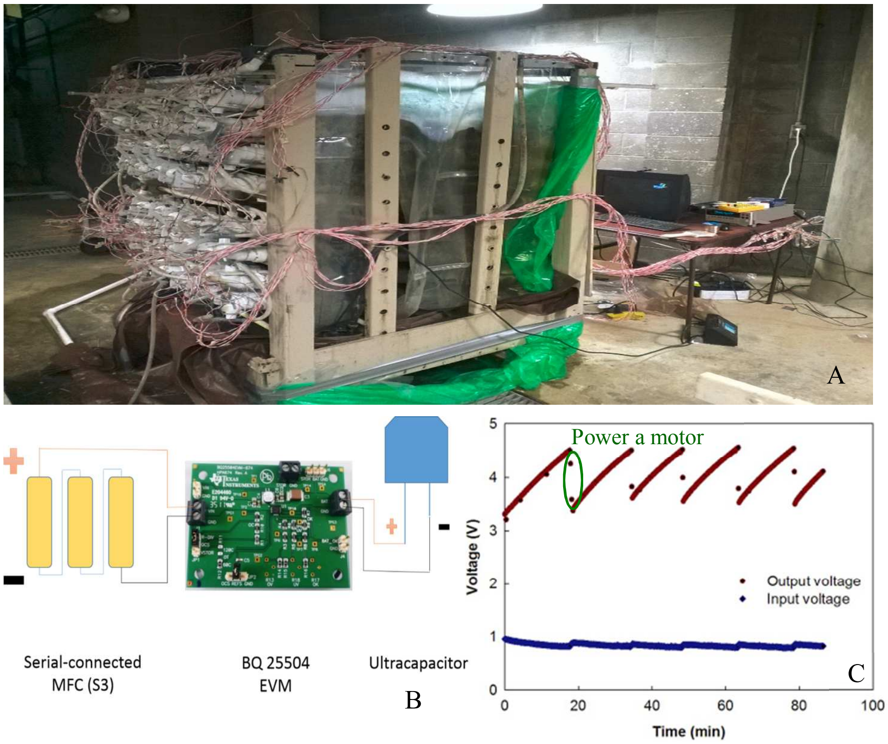

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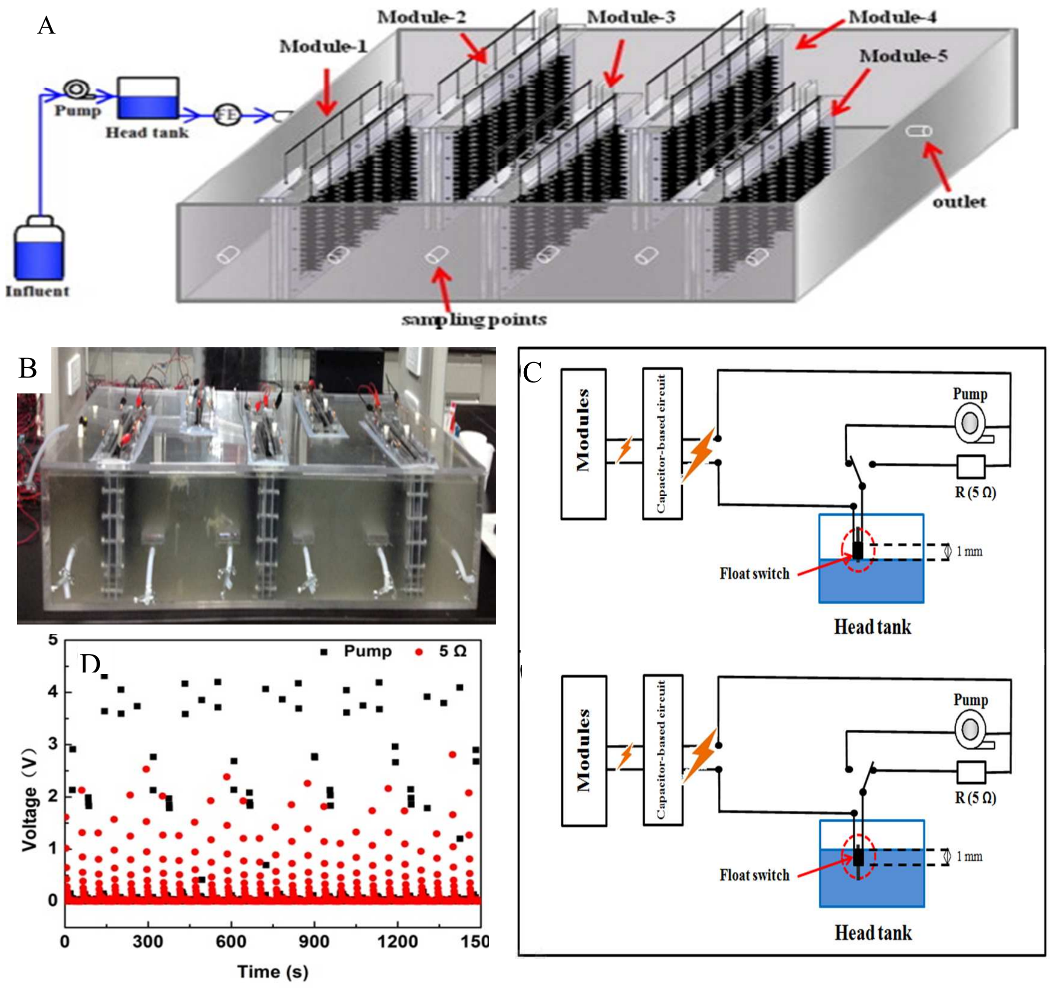

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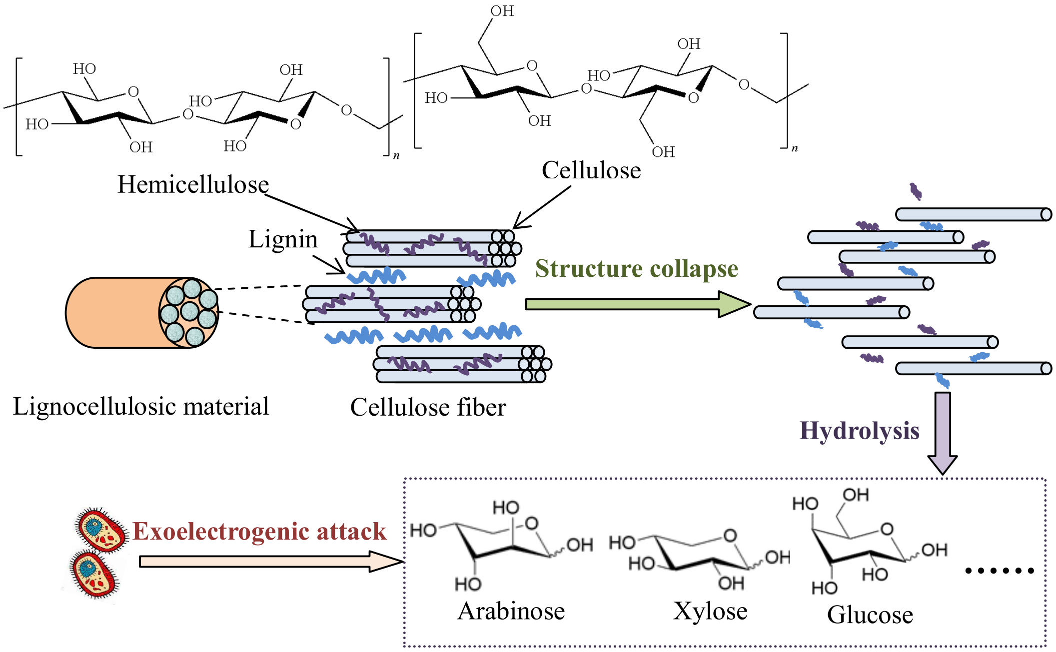

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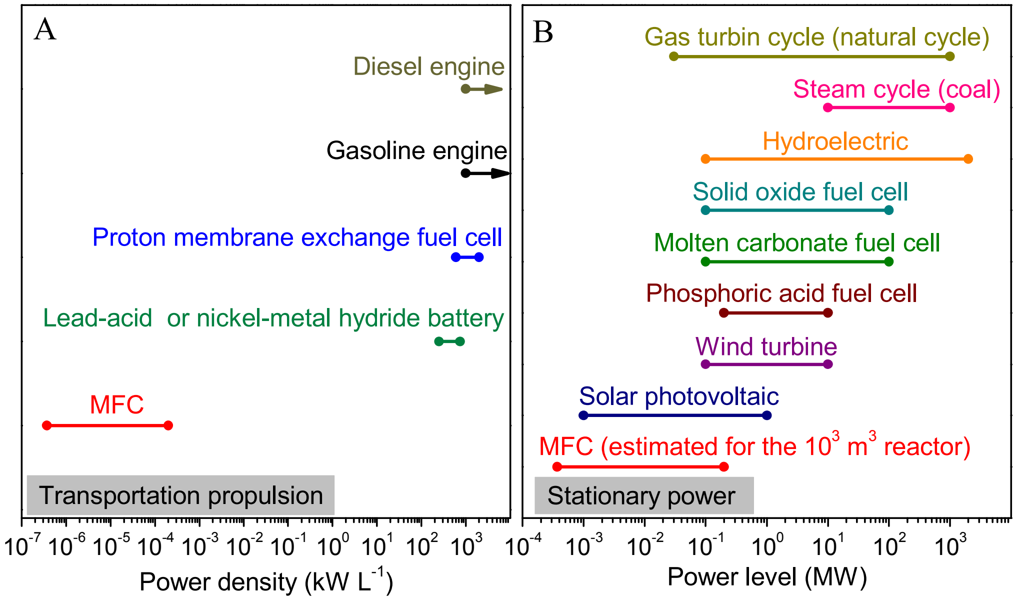

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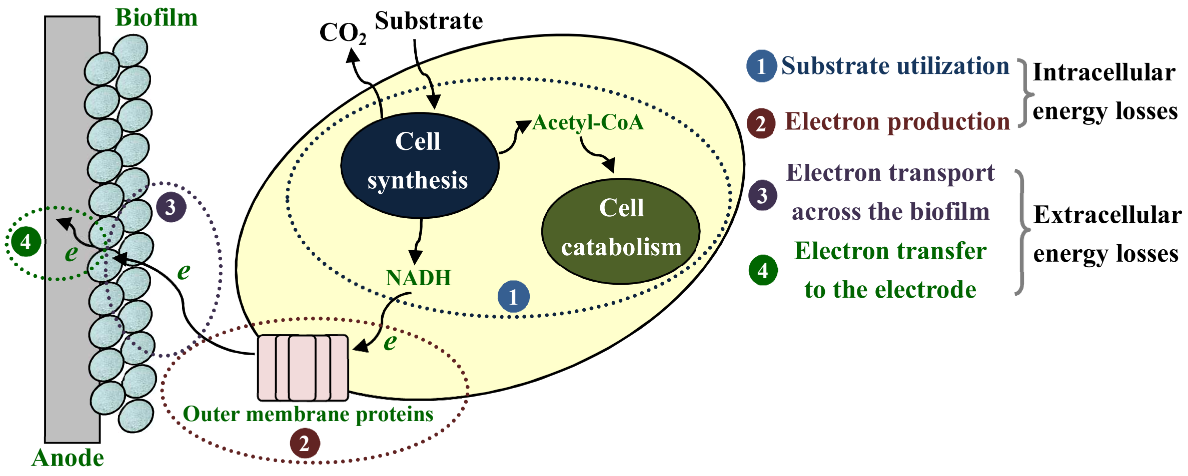

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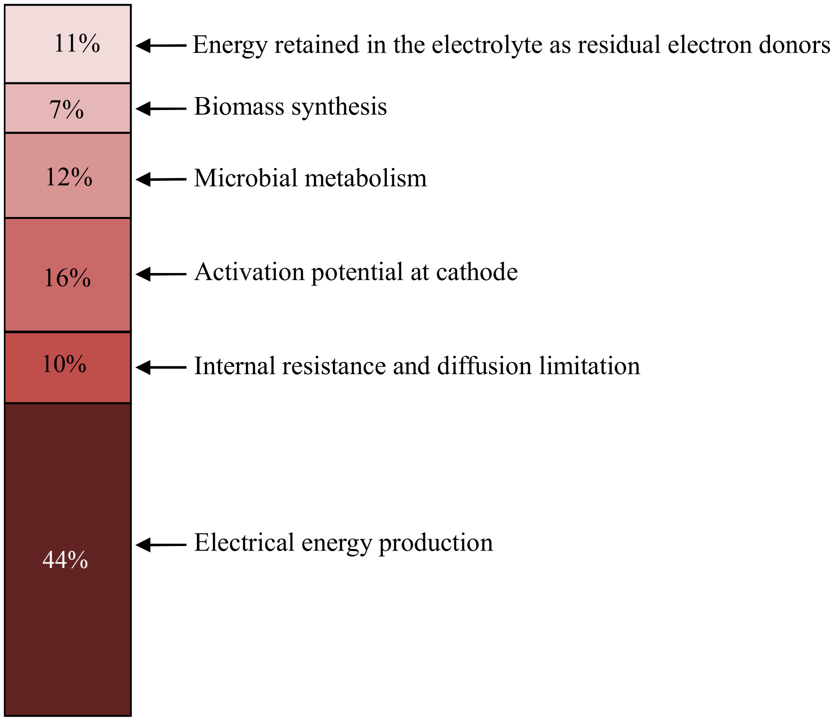

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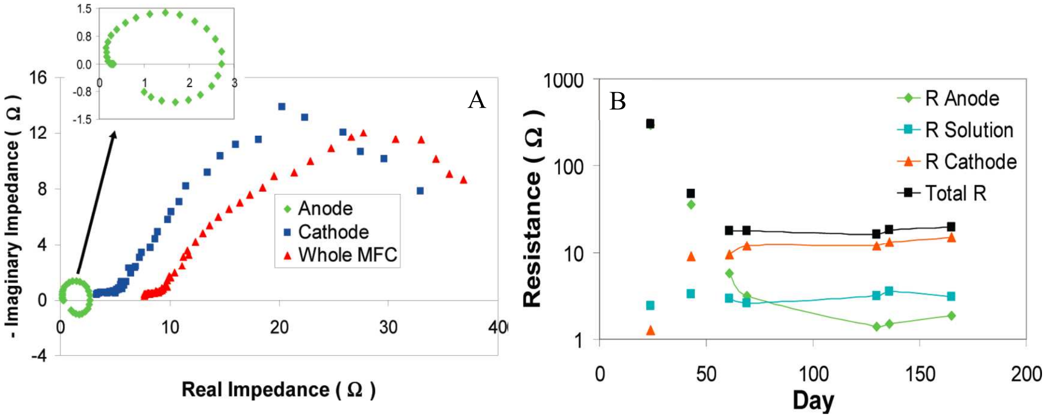

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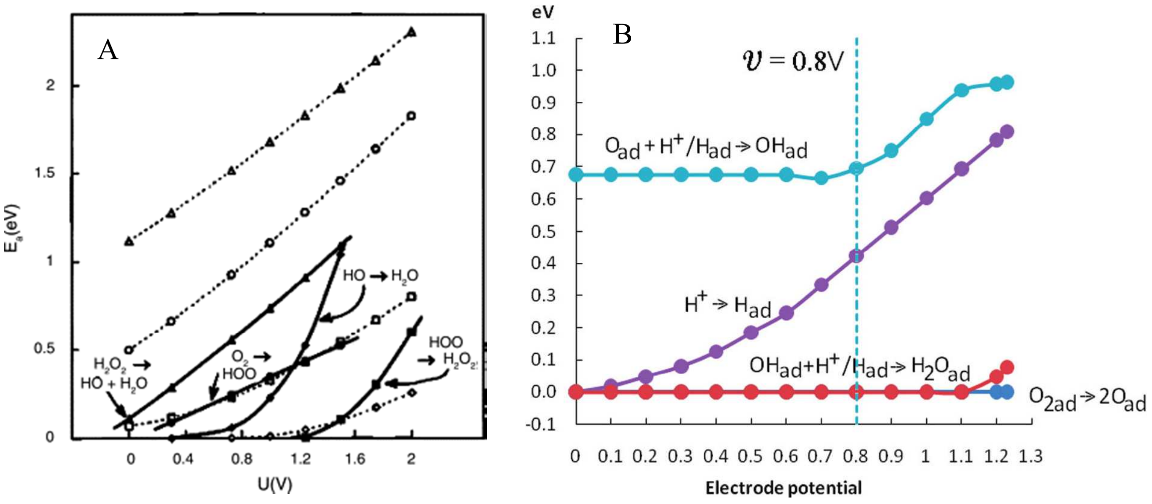

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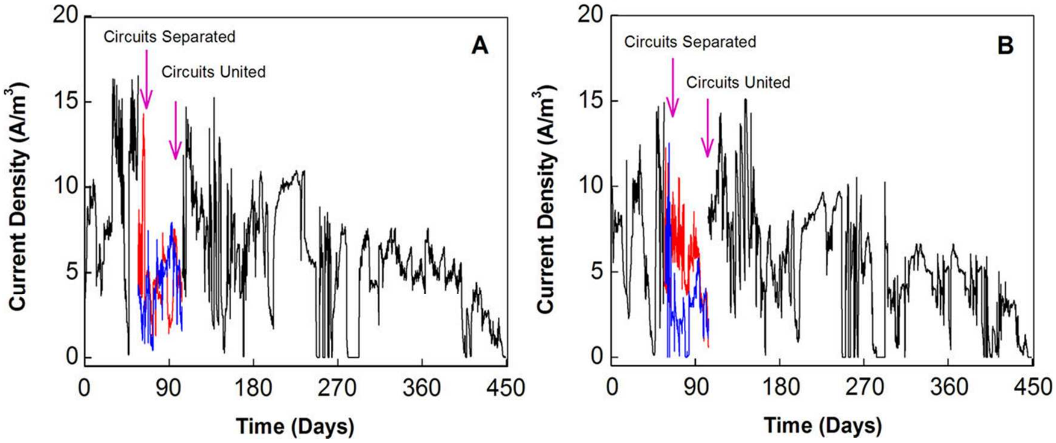

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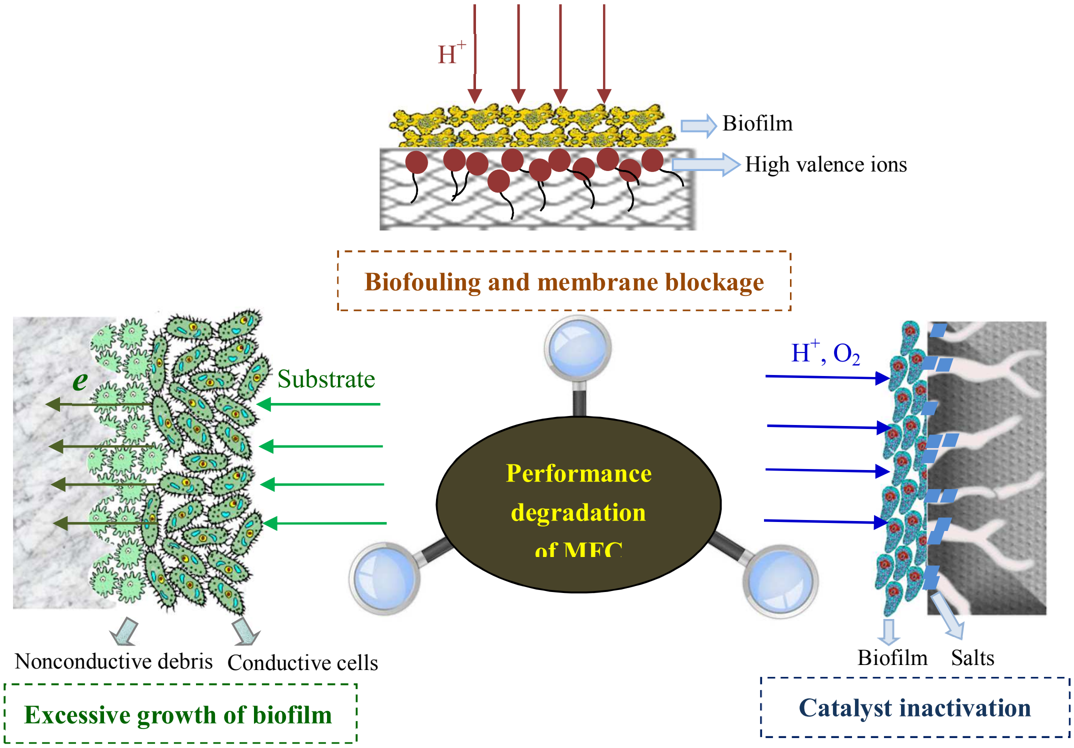

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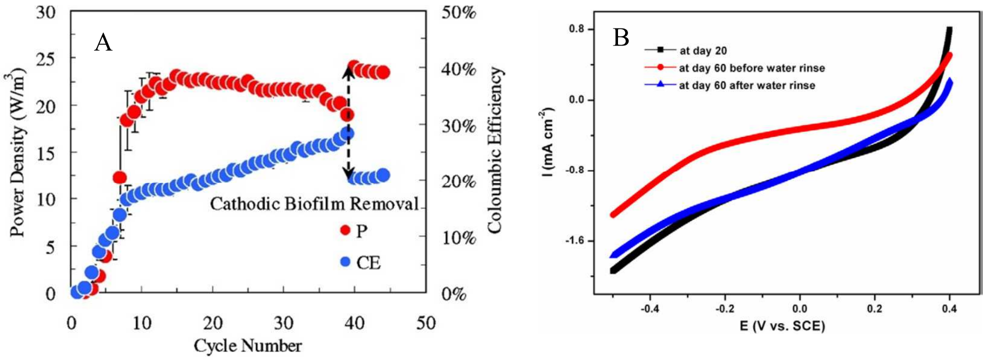

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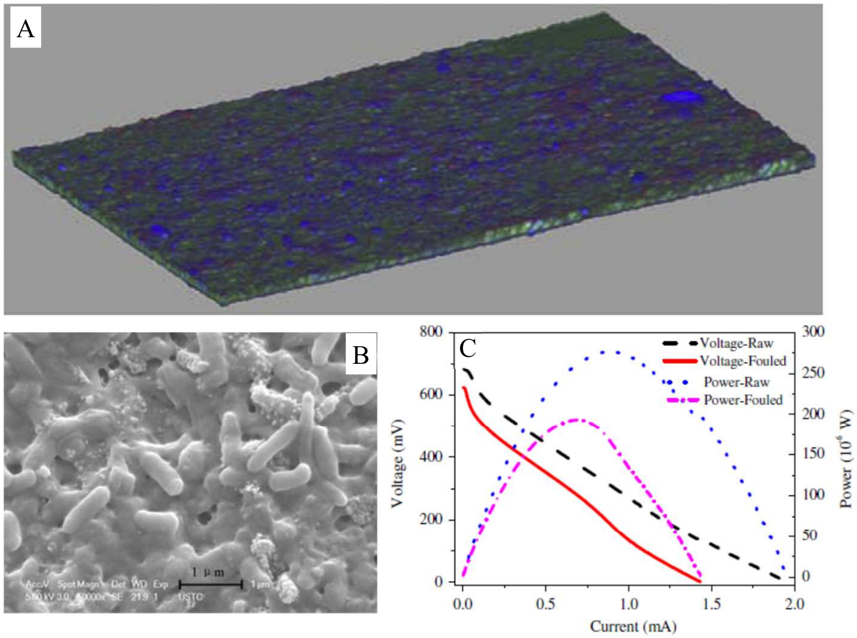

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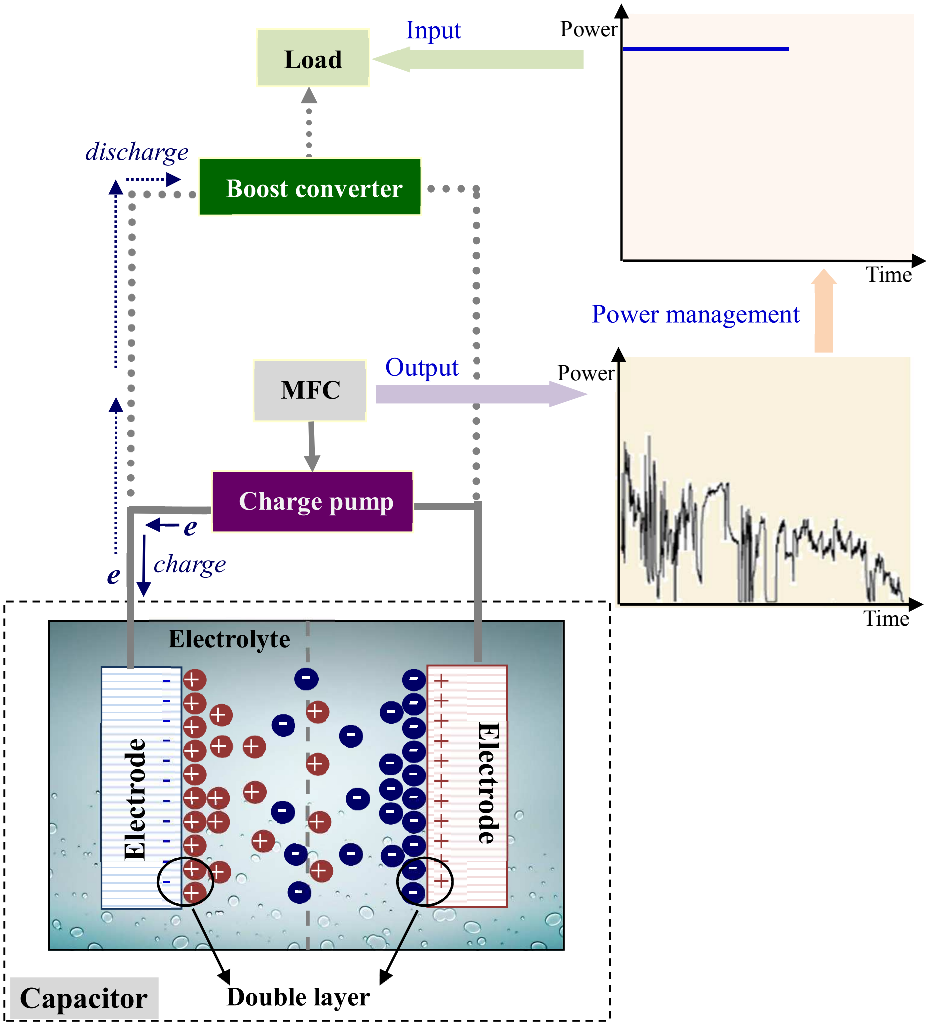

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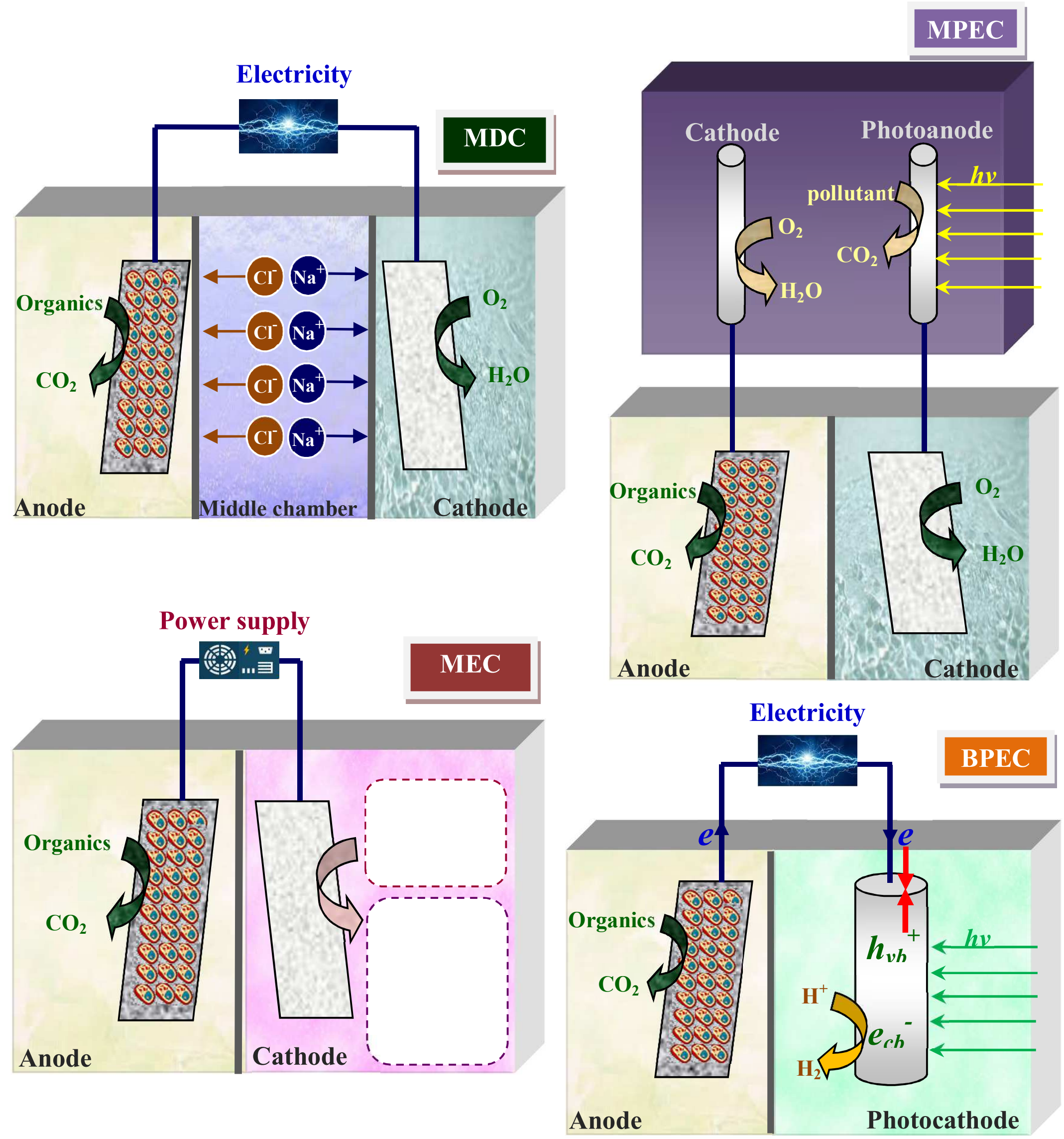

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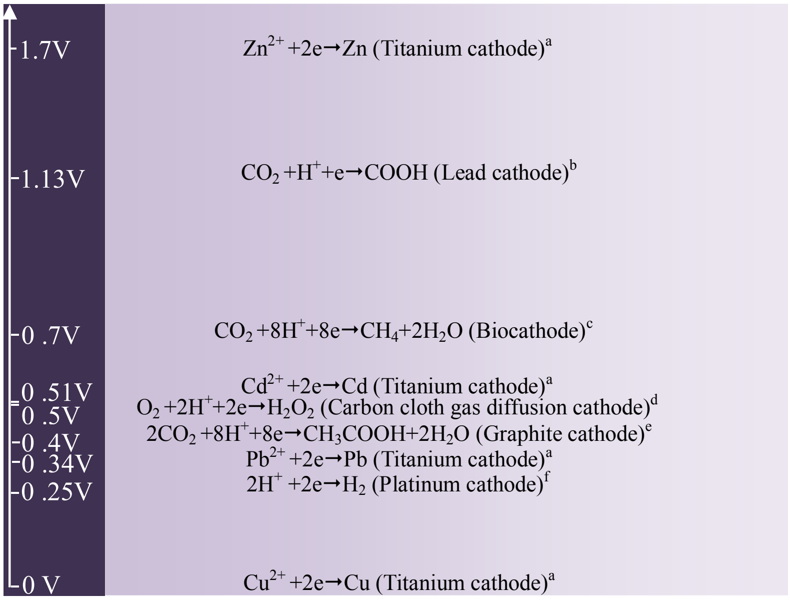

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