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Review—Microbial Electrosynthesis: A Way Towards The Production of Electro-Commodities Through Carbon Sequestration with Microbes as Biocatalysts

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There has been a considerable increment in the atmospheric CO_2 concentration, which has majorly contributed to the problem of global warming. This issue can be extenuated by effectively developing microbial electrosynthesis (MES) for the sequestration of CO_2 with the concurrent production of biochemical and biofuels. Though the MES technology is in its infancy, it has exhibited enormous potential for sustainable mitigation of CO_2 and bioelectrosynthesis of multi-carbon organic compounds. The problem of storage of excess renewable electrical energy by conventional means can also be alleviated by employing MES, which stores it in the form of C–C bonds of chemicals. This review focuses on the various aspects of MES and recent developments made in this field to overcome its bottlenecks, such as the lower yield of organic compounds, separation of products of higher chain organic compounds, etc. In particular, the microbial catalysts and cathode materials employed in MES have also been emphasized. Keeping in mind the potential of this innovative technology, researchers should focus on improving the yield of MES by developing novel low-cost cathode materials and discovering efficient and robust micro-organisms, which would be a significant step forward towards the further advancement of this technology.

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The increased CO_2 emissions leading to the rise in the average global temperature is the most concerning global problem for the environmentalists nowadays. Greenhouse gases (GHGs) are the culprit of this emergent problem of global warming. Among the GHGs, the contribution of CO_2 (greater than 30 Gt year^{-1}) is 63%, which is quite high.[1] Hence, the use of different CO_2 capture and storage techniques have come into the fray in the last decade. Two utilisation approaches, namely direct utilisation of CO_2 and conversion of CO_2 into chemicals and energy products, have emerged. Among these two, microbial electrosynthesis (MES) comes in the latter category, where bioelectrochemical techniques are applied for the conversion of CO_2 into value-added products using electricity as the energy source.[2,3]

The MES is an innovative technology, which offers the benefit of (i) generating multi-carbon organic compounds, named as electro-commodities, from sequestration of CO_2 by employing anaerobic electrotrophic microbes as biocatalysts, and (ii) storage of excess electrical energy in chemical bonds.[2,4] Due to the thermodynamic stability of CO_2, external energy needs to be supplied to carry out its activation and subsequent conversion reactions. A typical MES setup consists of two chambers, namely abiotic anodic chamber and biotic cathodic chamber; separated by a proton exchange membrane (PEM) that allows the protons to migrate from the anodic to the cathodic chamber (Fig. 1). At the anode, water molecules split into protons, electrons, and gaseous oxygen. The oxygen escapes the anodic chamber, protons are transferred to the cathodic chamber through the PEM, and the electrons are drawn to the cathode through an external circuit. In the cathodic chamber, the electrons and protons or energy carriers such as hydrogen (H_2) and CO_2 are combined by biocatalysts to produce primarily volatile fatty acids (VFAs) like formate, acetate, butyrate, etc.[5] through H_2 mediated electron transfer or direct electron transfer (DET) processes, which is not mediated through H_2 route. The process of MES mimics the natural photosynthesis process if the external electrical energy is supplied from a source of solar energy.[6] Generally, the acetogens, which follow the Wood-Ljungdahl (WL) pathway for CO_2 fixation, have been used as biocatalysts at the cathode of MES systems. Hence, acetate has mostly been reported to be the main product of MES. Nevertheless, other organic chemicals with higher carbon content, like propionate, butyrate, ethanol, isopropanol, caproate and caprylate have also been reported to be synthesised from CO_2 fed via MES.[7–10]

Electro-commodities is a homologous term used to refer to these chemicals, which are commodity chemicals, that are produced from the reduction of CO_2 by microbes. The energy required in the process is generally supplied in the form of electrical power through an external power source. Thus, MES could help in reducing the dependency on non-renewable resources like crude oil and thereby shift the focus from the production of the naphtha-based chemicals to the renewable energy-based chemicals.[11] The process of MES is carbon neutral, and therefore can be considered as the process for the future.[12] It can become a viable option to counter the numerous emerging environmental problems arising due to the elevated atmospheric CO_2 concentration.

The use of MES for the production of organic chemicals by reducing CO_2 has numerous advantages (Fig. 2). The technology doesn't require cultivable land for the production of biofuels, which is a major advantage in countries where there is an acute shortage of land.[13] Moreover, the efficiency of MES combined with a photovoltaic system is comparatively higher than biological photosynthetic pathways. Hence, a high quantity of valuable products can be synthesised by using less amount of energy through MES.[14] The process of MES also doesn't require the addition of huge quantities of nutrients and high-quality water in the setup, thus reducing operational costs. It also doesn't release excess nutrients and other pollutants into the ecosystem, thus rendering it as a sustainable and eco-friendly process. Another major benefit of synthesising electro-commodities using MES is that the requirement for downstream processes is not as high as that of biofuels production from biomass. The extraction of biofuels from biomass adds extra costs to the process and it also generates additional wastes, demanding further mitigation strategies.[15]

The thermodynamic stability of CO_2 is very high, and thus an enormous amount of energy is required for cleaving its double

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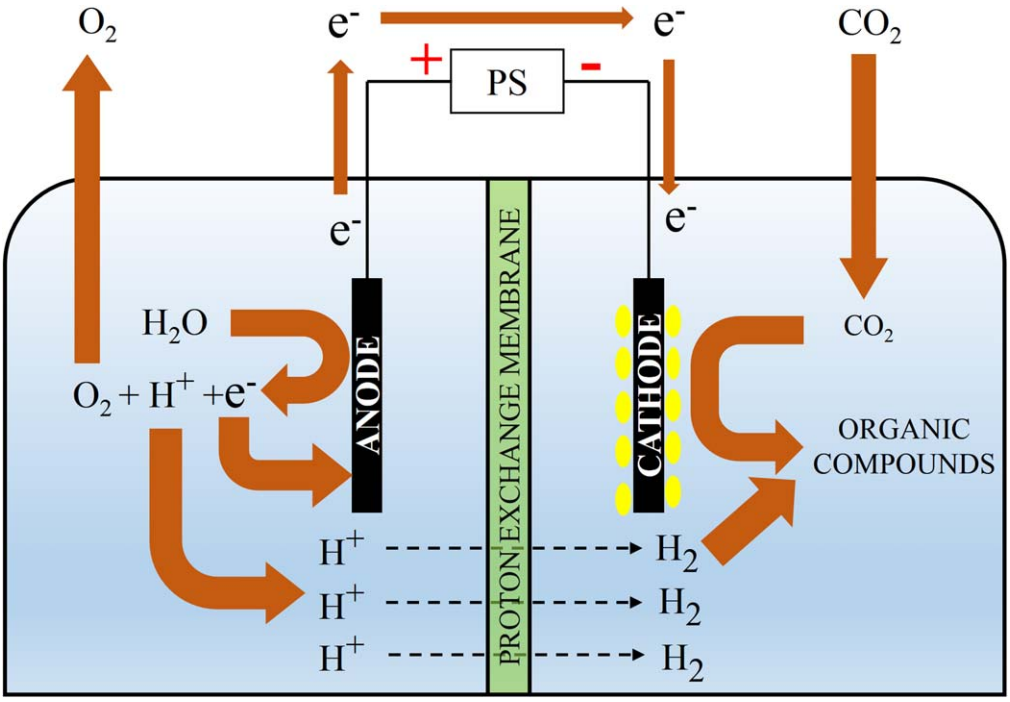

Figure 1. Schematic of a typical microbial electrosynthesis system and the processes involved therein.

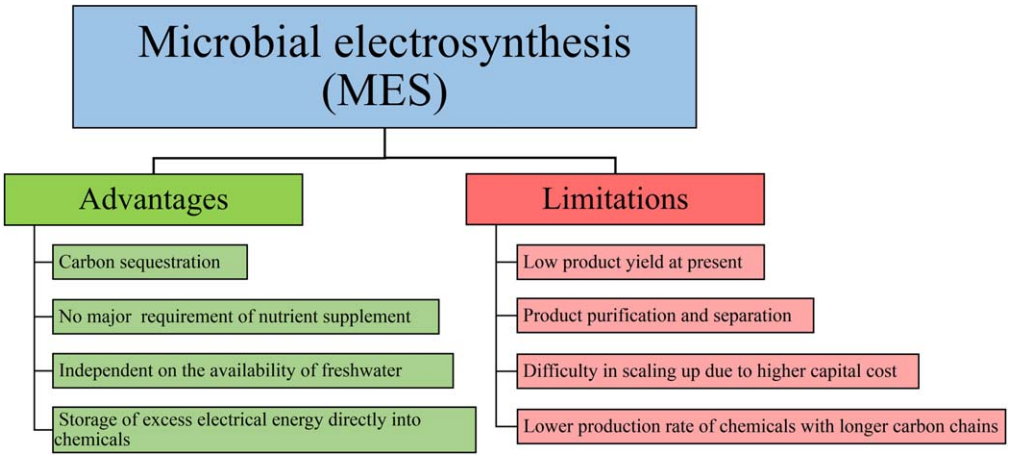

Figure 2. Major advantages and limitations of microbial electrosynthesis system.

bonds.[16] The energy required for the process of cleaving the bonds can be reduced by implementing metal catalysts.[17] However, the economic feasibility of the process is then compromised. This bottleneck can be circumnavigated by replacing the expensive catalysts with biocatalysts that are not only cost-effective but also don't require regular maintenance. Biocatalysts can either be enzymes or microbes. Specific enzymes can be used depending upon the intended product and reactor configuration.[18] The microbes that reduce CO_2 into organic compounds by taking up electrons or reducing equivalents from the electrode are known as electroautotrophs.[19] Such microbes can grow both in the form of biofilm at the electrode surface or planktonic cells in the bulk phase. Hence, the use of biocatalysts to reduce CO_2 can lessen both the operational and capital cost of the process.

This article encompasses various aspects of MES and the challenges encountered in scaling-up of the process. It focuses on the application of different cathode materials and biocatalysts employed in the process. The recent advancements in terms of products synthesised and respective yields are also presented. Finally, the economic feasibility and the applicability of the process for the production of biochemicals and biofuels with concomitant carbon sequestration are discussed.

Cathodic Microbial Electron Transfer Mechanisms

The transfer of electrons from the cathode to the microbes plays an imperative role in the efficiency of MES. Grossly, there are two mechanisms for the transfer of electrons from the cathode surface to the electrotrophs, namely, direct and indirect electron transfer mechanisms. The DET or non-H_2 mediated electron transfer generally occurs when there is a direct contact between the microbial cells or biofilm and the cathode. The electrons are taken up directly by the cells via redox-active proteins like c-type cytochromes. If more than one layer of cells is present on the electrode, then the electrons are conducted through the intermediate cells to the outermost cell.[20] Furthermore, electrons can also be transferred through externally added electron mediators like quinone, Fe or other metals[21,22] or through the mediators, such as flavin, pyocyanin,

thionine, etc., secreted by some of the microorganisms.[23–25] The major benefit of DET is that the probability of loss of electrons in the electrolyte is negligible, thus increasing the faradic efficiency of the process. Also, the loss of biocatalysts is insignificant when a continuous mode of operation is used. Due to the biofilm attachment on the electrode surface, the diffusion coefficient decreases, which in turn increases the inherent resistance of the cathode. Several such diffusion limitations come into play consequently, minimising electrode-electrolyte interaction. Moreover, the diffusion of products out from the biofilm to the electrolyte also decreases, thus apparently diminishing the yield of the system.[26] Unfortunately, this DET mechanism is yet to be convincingly proven in a MES.

The other mode of electron transfer is mediated through numerous electron shuttles, which is mostly applicable to planktonic cells that remain in suspension in the catholyte.[27] The electrons can also be mediated through molecules of H_2, soluble or insoluble mediators and capacitive particles.[28] The mediators could be synthesised by the microbes itself, like the derivatives of phenazine and flavin,[29] or can be added externally like quinones and viologens[30] to enhance the electron shuttling process. The externally supplemented mediators could have a toxic effect on the microbial catalysts, and thus the addition of such chemicals in BESs is generally avoided. Moreover, the dependence of the system on the concentration of mediators makes the process disadvantageous. As the cells are in a suspended form, their retention in the cathodic chamber becomes a significant problem for continuously operated systems. Furthermore, there could be various losses if the reducing equivalents are unable to come in contact with the suspended cells, thus adversely affecting the performance of the system.[31] On the contrary, the mediated electron transfer mechanisms can be useful when the products synthesised are stored in the cells itself, and the biomass needs to be harvested for the extraction of these products. For such cases, the ease of removing the planktonic cells from the system could become beneficial. However, the separation of mediators may be required, which again adds on to the operational cost of the system.

For MES, the cathode being negatively charged and likewise for the biofilm, the electrostatic force of repulsion averts the attachment of the microbes onto the cathodic surface. However, this can be overcome by employing positively charged cathode materials, which can instigate a better degree of microbial attachment.[32] However, the H_2-mediated route is generally observed in these systems because of the employment of lower cathodic imposed potential (<-0.4 V vs standard hydrogen electrode under standard conditions), which favours the H_2 evolution reaction. Due to various losses associated with indirect electron transfer mechanism, coulombic efficiency is usually less in these cases as compared to DET-based bioproduction.[13] The choice of any of the above mechanisms is majorly dependent on the product intended to be produced, the microbial inoculum source, set or applied cathode potential, and the operational mode of the system.[33] It is important to mention that for continuously operated systems, DET might be more useful, and for batch processes, both the mechanisms could be efficiently used.

Microbial Biocatalysts used and Products Recovered

Chemolithoautotrophic microorganisms are generally employed to fix CO_2 into various organic compounds in the presence of H_2. The biocatalyst can be in the form of a biofilm, i.e. attached to the cathode; or it can be planktonic or both. A DET takes place when an electroactive cathodic biofilm is present, and for planktonic microbes, electron transfer is mediated through H_2.[34] Similar to other chemical reactions, the efficiency of bioelectrochemical reactions is also affected by biocatalysts used in the process. These biocatalysts can be in the form of either pure culture or mixed culture, where multiple species are present in a syntrophic association with each other.

Several types of pure microbial cultures mainly belonging to *Clostridium* and *Sporomusa* genera have been used for the synthesis of organic compounds from CO_2 in MES (Table I). Other examples include, *Trichococcus palustris*, *Desulfotomaculum*, *Oscillibacter*, *Clostridium celerecrescens*, *Clostridium propionicum*, *Tissierella*, etc.[35] In terms of the performance of pure culture, *S. ovata* has been observed to be the most performant species with the highest production rate of acetate.[36] The use of mixed cultures has also been well demonstrated not only in MES but also in other types of bioelectrochemical systems.[37,38] Acetate is the most prevalent product of MES both for the mixed and pure cultures as acetogens dominate in these systems.[39] However, the yield of acetate for MES inoculated with pure culture is generally observed to be higher in comparison to the yield from a MES inoculated with a mixed culture. Such a phenomenon could be attributed to the presence of parasitic microbes in the mixed culture, which would consume the product or use the electrons in non-targeted reactions for the formation of numerous by-products.[40] For example, the presence of methanogens in the mixed consortia diminishes the yield of acetate considerably by consuming the electrons for the formation of methane through electromethanogenesis.[41]

For field-scale operations, aseptic conditions are difficult to maintain and therefore, mixed culture inoculum is mostly preferred in field-scale setups.[52] However, due to the lesser yield for mixed culture inoculum, researchers are enriching mixed consortia with performant pure culture following bioaugmentation, which when applied in MES as inoculum could lead to higher product yield. Multiple strategies have been used for enriching the mixed inoculum to enhance the production of electro-commodities.[50,53] Long-term sustainability of the biocatalysts in MES, collected from brewing wastewater was also demonstrated by Marshall, et al.[54] The biocathode in the previous investigation was colonised by *Acetobacterium, Sulfurospirillum* and *Rhodobacteraceae* species, which led to the acetate production at the rate of 17.25 mM d^{-1}.

Mixed cultures collected from different sources, such as domestic wastewater sludge, bog sediment, brewery wastewater, etc., have also been employed as biocatalysts in MES and promising results were obtained. Acetate yield of 19 g m^{-2} d^{-1} was observed for a MES inoculated with sludge collected from an upflow anaerobic sludge blanket (UASB) reactor effluent, which is very high in comparison to the yield obtained in other investigations. Application of genetic engineering to produce butyrate from CO_2 and H_2 using *Clostridium ljungdahlii* as biocatalyst was also reported recently.[55] Therefore, the integration of genetically modified microbes with MES can lead to the production of more specific compounds with higher market value. However, the yield of MES needs major improvement, which would be a major step towards the commercialization of the process.

As acetogens are quite robust in growing in mild acidic and mild alkaline environments and can also use both autotrophic and heterotrophic metabolism, they are generally preferred in MES.[56] Acetogens are also capable of using CO as the only carbon source to produce organic molecules through the WL pathway. This pathway is also quite energy-efficient, which makes the process more lucrative.[57] Electro-commodities with longer chains like propionate and butyrate have also been reported to be produced in MES.[51] Butyrate can be produced as a by-product during bioelectrosynthesis of acetate from CO_2, and such an observation was reported by Ganigué, et al.[58] Other derivatives of butyrate, namely 2-oxo-butyrate and isobutyrate were also reported to be produced simultaneously with acetate using mixed culture inoculum in MES.[51,43]

The C3 compound, propionate, was also reported to be produced when bicarbonate was used in the catholyte[37] The production of alcohols through the fixation of CO_2 could make the process economically more feasible owing to the higher market value of these commodity chemicals. For the formation of these compounds, a reducing environment is required in the cathodic chamber of MES,

Table I. A comparative overview of different microbial catalysts used and products synthesized via MES.

Biocatalyst used	Imposed/Applied potential at cathode (V vs SHE)	Products synthesized	Production rate of acetate (g m^{-2} d^{-1})[b)]	References
Sporomusa ovata	−0.69	Acetate, H_2	51.1	42
S. ovata	−0.40	Acetate	13.51	36
S. sphaeroides	−0.40	Acetate, 2-oxobutyrate, formate	0.062	43
S. silvacetica	−0.40	Acetate, 2-oxobutyrate, formate	0.045	51
Clostridium aceticum	−0.40	Acetate, 2-oxobutyrate, formateAcetate, 2-oxobutyrate, formate	0.006	51
C. ljungdahlii	−0.40	Acetate, 2-oxobutyrate, formate	0.14	51
Moorella thermoacetica	−0.40	Acetate, 2-oxobutyrate, formate	0.104	51
Acetobacterium woodii	−0.69	Acetate	12.8	44
C. ljungdhalii	−0.69	Acetate, ethanol, H_2	7.51	45
S. acidovorance	−0.69	Acetate	10.4	46
S. malonica	−0.69		10.7	
S. ovata	−0.40	Acetate, 2-oxobutyrate	1.38	15
S. ovata	−0.66	Acetate, H_2	8.2[a)]	47
Mixed culture from brewery wastewater sludge	−0.60	Acetate, H_2, formate	38	48
Mixed culture from domestic wastewater treatment plant sludge	−0.85	Acetate, H_2, CH_4	16.3	49
Mixed culture collected from bog sediment	−0.40	Acetate, ethanol, butanol, butyrate, H_2, propionate,	0.0063	35
Enriched mixed culture from UASB reactor	−1.26	Acetate, H_2	19	50
Mixed culture from anaerobic digester sludge	−0.60	Acetate, CH_4	2.7	14
Mixed culture from septic tank	−1.10	Acetate, isobutyrate, propionate, 2-piperidinone	21.60 ± 1.87	51
Mixed culture from septic tank	−1.00	Acetate, butyrate, propionate	2.96 ± 1.65	33
Enriched mixed culture from anaerobic digester	−0.80	Acetate, H_2	108	13
Mixed culture from septic tank	−0.90	Acetate, isobutyrate, propionate, 2-piperidinone	3.09 ± 0.19	7

a) Value calculated from the data reported in the article b) Cathode surface area-based production rate, UASB-upflow anaerobic sludge blanket, SHE: Standard hydrogen electrode.

which could be achieved by maintaining a lower pH or a higher concentration of H_2.[59] With an imposed potential lesser than −0.4 V vs standard hydrogen electrode (SHE) at the cathode, simultaneous production of ethanol and acetate by the mixed culture inoculum has been reported.[35]

The long-term operation of MES can increase the concentration of acetate in the cathodic chamber, which would lower the pH and thus, alcohol production can be stimulated.[13] The production of polyol, i.e. glycerol by the reduction of CO_2 by *Geobacter sulfurreducens* in the presence of succinate and with a reduction current of 30 A m^{-2} was also demonstrated by Soussan, et al.[60] In another demonstration, the application of gas diffusion electrodes resulted in the formation of 21 g l^{-1} of alcohols (ethanol and butanol) and 13 g l^{-1} volatile fatty acids over a period of 90 d.[61] Not only liquid compounds were produced by the process of CO_2 reduction in MES, but also various gaseous products, like CH_4 and H_2, were reported to be produced simultaneously. Due to electro-methanogenesis, methane was found to be produced in the cathodic chamber, when mixed culture inoculum was used without any treatment to suppress methanogens.[41] Furthermore, H_2 is also abiotically produced in MES when protons combine with each other, thus aiding the indirect transfer of electrons from the electron-donating cathode to the microbiome. Therefore, MES has enormous potential as it can be used to produce a wide range of organic compounds by fixing CO_2.

Downstream Processing Approaches in MES

The boon of MES to produce multiple organic compounds also invites the need to employ further downstream processes to separate the target compound from the catholyte containing bacterial cells, nutrient media and other organic by-products. In this regard, researchers have come up with different innovative techniques to separate the target product mainly acetate, from mixed catholyte. For instance, anion exchange resin was employed to extract acetate from the catholyte of MES. Around 10 to 20 mg of acetate per gram of anion exchange resin was absorbed in 24 h from the catholyte broth containing multiple compounds.[62] In another demonstration, hollow fibre membrane made up of polypropylene was used to separate butyrate from the catholyte.[9] This membrane extracted 252.4 millimolar of carbon per litre as butyrate with butyrate: acetate ratio of 16:4.[9] Though traces of acetate were found in the extracted solution; however, successful separation of the target compounds was elucidated in this investigation.

Separation of acetate from the catholyte in a single setup was also explained by some researchers, where an extraction chamber was sandwiched in between the anodic and the cathodic chamber to separate acetate from the catholyte. The extraction chamber was separated by anion exchange membrane and PEM from the cathodic and anodic chamber, respectively; therefore, only allowing acetic acid to be accumulated in the extraction chamber. The acetic acid production rate from this setup was noted to be 19.2 g m^{-2} d^{-1} with a coulombic efficiency (CE) of 25.4%.[63] Simultaneous production and separation of acetic acid in a single setup is advantageous as the capital and operational cost of multiple setups can be avoided, thus rendering economic sustainability to the process of MES. However, the yield of MES from such three-chamber setups needs to be improved considerably so that it can pave the way towards the efficient field-scale implementation of the process.

Implications of Cathode Materials

In MES, cathode donates electrons or reducing equivalents to the microbes, which can be either present in the planktonic form or attached on to the cathode surface. The type of cathode material has an imperative role in the performance of the MES process. In general, the cathode material should offer high conductivity to conduct electrons from the cathode surface to the microbes and excellent (electro)chemical stability to prevent the chances of any parasitic reactions.[64,65] It should have a high mechanical strength to maintain its integrity during the flow of catholyte for continuous systems. Moreover, the cathode surface should be biocompatible to facilitate the attachment of microbes on its surface. The specific surface area should also be as high as possible to escalate the chances of bacterial attachment and activity.[36] Finally, low-cost cathode materials should be targeted for scaling up of MES, which would render this technology economic sustainability.[66,67]

As this technology suffers from a major bottleneck of low productivity, researchers are focusing on exploring novel and composite cathode materials to counter the same. The use of various commercially available materials, newly fabricated materials, and modified commercial materials have been reported in the recent past. These materials aim to improve the surface area and surface chemistry besides electrocatalytic activity and biocompatibility, thus leading to enhanced bacterial and electrode interactions, which in turn enhances the adhesion of microbes to the cathode surface.[68] Improved biofilm formation shifts the electron transfer mechanism towards direct route from H_2-mediated one and results in increased electrocatalytic activity in terms of electron uptake and lowering the H_2 evolution overpotential.[69,70] The research on the cathode materials thus far suggests that the three-dimensional cathodes with higher biomass retention can improve the yield of the H_2-based process in MES systems.

To date, researchers have majorly used carbon-based electrodes for the bioconversion of acetate from CO_2. The inherent properties like biocompatibility and higher specific surface area of carbon-based materials, make them a suitable material for application as biocathodes in MES. Also, these materials offer less mass transfer resistance, thus increasing electrode-electrolyte interaction. Nevin, et al.[15] demonstrated the first proof of concept of MES from CO_2 using a negatively poised graphite cathode as an electron donor. After this pioneering study, researchers have carried forward the work on MES by using various types and shapes of carbon-based electrodes, like carbon rod[35] or stick,[17] carbon plate, and cloth,[58] reticulated vitreous carbon (RVC),[71] etc. (Table II). However, owing to the low porosity and low electroactive available surface area of the graphite rod, the product yield of the system gets limited.

To overcome such limitations, Marshall et al. used granular graphite as a cathode and achieved a high volumetric acetate production rate of $>$ 4 mM d^{-1} and 1.04 g l^{-1} d^{-1}, respectively.[54,79] During the operation of MES, the cathode is negatively charged, and during inoculation, when the cathode is not poised, it is neutrally charged. The typically used carbon-based cathode materials are also uncharged.[80] On the other hand, the acetogenic gram-negative microbes like *S. ovata* possesses a negatively charged outer surface.[81] Thus, this electrostatic force of repulsion between the cathode surface and the microbes inhibits bacterial attachment on the cathode surface. Hence, the impregnation of positive charge onto the cathodic surface could improve cathode-bacterial interaction leading to enhanced biofilm growth. This methodology was utilised by different scientists and at the same time, higher yield was achieved as compared to unmodified cathodes.[36] Chemical agents like chitosan, cyanuric chloride, poly-aniline, melamine, etc. and metals like gold, palladium and nickel were used by Zhang, et al.[36] to induce positive charge onto the surface of the cathode, thus improving the yield of acetate through MES. Chen, et al.[66] also used a similar technique, where carbon cloth was modified using reduced graphene oxide and positively charged tetraethylene pentamine nanoparticles leading to the formation of a highly structured biofilm.

Numerous other materials with customised surfaces have also been tested to proliferate biofilm attachment. For instance, the use of porous Ni-nanowire graphite as cathode material considerably improved (2.3 times) the acetate production rate over untreated electrodes.[82] In MES, the concentration of H_2 could limit the production of electro-commodities. This limitation could be resolved by using stainless steel on carbon felt, which increases H_2 production, thus increasing the overall yield of the system.[83] The use of unmodified RVC foam as cathode material in MES has also been

Table II. Some representative cathode materials used in MES and yield of acetate obtained.

Cathode material	Applied potential (mV vs SHE)	Current density (A m^{-2})	Acetate production rate (g m^{-2} d^{-1})	CE in acetate (%)	References
Carbon rod	−201	4.1	0.0431	NR	72
RVC foam	−1100 to −1300	83.3	196.8	35	71
Carbon felt	−853	3.3	16.3	24	49
Graphite felt	−795	10	16.57	50	13
Carbon paper	−690	0.37	4.9	4.9	73
Graphene paper	−690	2.5	39.8	90.7	73
Carbon cloth-reduced graphene oxide tetraethylene pentamine	−690	0.23	62.4 ± 26.64	83 ± 3	66
Nanoweb 3D RVC	−850	37	195 ± 30	70 ± 11	74
MWCNT-RVC	−1100	200	1330	84 ± 2	75
Chitosan-coated carbon cloth	−400	0.47	13.51 ± 3.30	86 ± 12	36
3D RVC with CNT	−850	102	685 ± 30	100 ± 4	76
Graphite granules	−600	12.3	2.7	28.9	14
Graphite felt	−1200	27	36	NR	77
Carbon felt	−850	175	376	87.6	8
Stainless steel	−1300	35	76	28	78
Carbon felt	−1400	5	11.5	63	69
Carbon felt	−1000	NR	2.96 ± 1.65	60.3 ± 3.1	33
Carbon felt	−900	65.65	3.09 ± 0.19	62.12 ± 3.6	7
Graphite felt	−1100	31.1	21.60 ± 1.87	68.81 ± 3.3	51

NB-SHE: Standard hydrogen electrode, CE: Coulombic efficiency, RVC: reticulated vitreous carbon, CNT: carbon nanotubes, NR: Not reported.

demonstrated.[71] The higher surface area of RVC, coupled with a continuous mode operation, improved the rate of acetate production up to 196.8 g m^{-2} d^{-1}.

Jourdin, et al.[74] demonstrated the use of NanoWeb-RVC cathode that significantly enhanced acetate production by 33.3 times as compared to the unmodified carbon plate electrode. Due to the high surface area and macroporous structure of NanoWeb-RVC, mass transfer limitation was minimised, thus improving electrode-electrolyte interaction, and subsequently enhancing bacterial attachment. The same group also developed CNT modified RVC electrodes and employed them with an acetogenic microbiome, which enhanced bioelectrosynthesis of acetate from CO_2.[76] The RVC electrodes were further modified using multi-walled carbon nanotubes (MWCNTs), and it resulted in an acetate production rate of 1330 g m^{-2} d^{-1}, which is the highest reported value for acetate production with respect to projected cathode surface area till date. In an interesting study, 3D carbon felt was modified using iron oxide, and 4.8 times increment in the yield of acetate was reported.[84]

The use of graphene-based electrodes for biotic electrodes is increasing day by day.[85] In this regard, 3D graphene carbon-based electrode was developed by Aryal, et al.[86] that lead to the generation of robust biofilm. The acetate production was enhanced by 6.8 times as compared to the MES using unmodified carbon felt in this study. The same research group also developed flexible and freestanding graphene paper cathodes, and reported about 8-fold increment in acetate production in comparison with the carbon paper electrode.[73]

Recently, composite electrode materials comprising of metals and carbon have been intensively applied for in situ hydrogen production in numerous investigations.[87] Numerous composite electrodes like nickel nanoparticles partially embedded in carbon fibre cloth, carbon–nickel composite, graphene oxide with Ni and Cu, Fe–Ni-graphene composite and perovskite-based electrodes have demonstrated excellent hydrogen production in electrochemical cells due to their excellent catalytic properties.[87–91] The application of hydrogen producing electrodes as cathodes in MES would significantly improve the yield of MES. The hydrogen produced in the cathodic chamber of a MES due to the application of these electrodes can assist in the efficient transfer of electrons from the cathode to the microbes, which in turn will improve the production rate of organic chemicals. The presence of carbon in these composite materials also improves the conductivity of the materials and renders them biocompatible making them suitable for the application as a cathode in MES. Thus, these materials should be tested as cathodes in MES and their performance should be evaluated.

To summarize, researchers are mainly targeting cathodes with a higher surface area, higher porosity, excellent conductivity, and biocompatibility. These features will not only trigger the formation of stable and robust biofilm , however, would also increase the electrode-electrolyte interaction leading to higher throughput. The use of 3D cathodes for MES seems to be a promising option in the long run; however, the focus should still be on the development of low-cost cathodes for MES that would pave the way towards scaling up of MES.

Techno-Economic Feasibility of MES

The MES technology is in its infancy, and more research efforts should be emphasized on enhancing the product titer and rates at higher coulombic and energetic efficiencies and scaling up of this technology. Cost-effective reactor design and the use of low-cost electrodes could considerably reduce the capital investment for the setups.[51,92] The feedstock used for MES is CO_2, which is abundantly available in the atmosphere, and thus, the cost associated with it is minimal. However, investments are still required to capture and purify the inlet gas. The cost of capturing CO_2 from the atmosphere can be diminished by feeding the flue gas of various industries directly into the cathodic chamber of MES.[93] The composition of flue gas emitted from different industries vary quite broadly and not only contain CO_2 but other toxic gases like H_2S, NH_3, SO_x, NO_x etc. and particulate matter.[94] These gases when come in contact with water produce acids or bases, which can significantly alter the pH of the catholyte, which in turn will have an adverse effect on the activity of the cathodic microbes and the electrode material. Moreover, the temperature of flue gas is also very high, which is also a concerning factor. Therefore, due to these characteristics and presence of poisonous gases in the flue gas, it could have an adverse effect on the bacterial community and electrode material of MES. However, this could be avoided by adding a few specific gas filters in pipelines leading to the system. On the other hand, the effluent contains a mixture of various products, which demands separation, thus adding on to the cost of production.[95] If the purity of the products formed can be achieved by using pure or genetically modified microbial strains, then the downstream cost can be reduced considerably.[96]

As discussed earlier, acetate is the most commonly produced chemical of MES from CO_2. It has widespread application as a raw material for the production of various petrochemical products, such as vinyl-acetate monomer, terephtalic acid, and ethyl acetate.[97] It is also used as a precursor for the preparation of latex emulsion resins, adhesives, finishing agents for textile products, cellulosic plastics, paper coatings, etc.[98] The global demand for acetic acid is also high and is expected to grow at a rate of 4.9% per year.[99] Traditional chemical processes like methanol carbonylation, oxidation of naphtha, direct oxidation of ethane, and biological processes like the fermentation of hydrocarbons are used to synthesise acetate. However, all these processes generate various by-products and thus require purification. Moreover, these processes use expensive chemical catalysts, and the reactors are made of robust and durable materials since the reactions take place at high temperature and pressure conditions. Hence, the overall cost of pure acetate escalates. Here the application of MES for the synthesis of acetate is beneficial because the biocatalysts that are used in the process do not require high temperature to operate and are not toxic to the environment.[15] The microbes used in the process are self-sustainable and periodic replacement of the same is not required. Thus, MES can provide an alternate, cost-effective route for the synthesis of acetic acid from CO_2.

The major drawback of MES is its low product titer, which considerably increases the cost of acetate production. To counter this problem, using large reactors is an option. However, it adds to the capital cost required for the field-scale application of this technology. Anaerobic fermentation (AF) is another biological pathway for the conversion of CO_2, CO, and water into acetic acid[100] using *Clostridium*.[101] A comparative study based on the economic feasibility of methanol carbonylation, direct oxidation of ethane, AF and MES demonstrated that molar yield of acetate via MES and AF should be enhanced considerably (267 thousand and 492 times, respectively) to compete with other well-established technologies.[97] Production and investment cost were found to be significantly higher for MES and AF owing to the lower yield of these technologies. However, the amalgamation of these two technologies resulted in the production of acetate at a competitive price (0.24 £ kg^{-1}), considering its present market value (0.48 £ kg^{-1}). It was also concluded from the study that bioprocesses could compete with industrial processes when used for the small-scale production of high valued chemicals.[97]

Prevalent CO_2 Sequestration Techniques and Their Industrial Applications

Innumerable industrial processes like welding, production of foaming agents, food and soft drink preparation, etc., and dry cleaning and packaging industries require CO_2 for their functioning.[102] However, the demand for CO_2 emerging from these industries is negligible, and therefore, the rate of utilization of CO_2 from these industrial processes has an insignificant effect on the

global carbon emissions. Few international firms are capitalizing on the easy availability of atmospheric CO_2 and are directly converting it into various usable chemicals or are capturing it for direct utilisation in their processes. For example, PRAXAIR and Great Point Energy are utilising CO_2 directly in numerous industrial processes; whereas, Novomer, Newlight, and Algenol are converting CO_2 to polypropylene carbonate, AirCarbon plastics, and ethanol, respectively.[85] Not only chemical means of CO_2 sequestration have been employed, however, few industries like Phycal^{TM} are following biological pathways of CO_2 sequestration by growing algae in ponds with CO_2. The algae grown in these ponds are further processed to produce biofuels and oils. Biofuels produced from these algae are expedient because the process doesn't require arable land and freshwater for agal cultivation, which is not the case for biomass-based biofuel production.

The technology of MES has added advantage over the electrochemical reduction of CO_2 as expensive metals catalysts are not required in this process.[103] The energy required for MES can be supplied from photovoltaic cells, and then the system would mimic photosynthesis. The use of CO_2 as feedstock possesses countless challenges owing to its inertness. Its lower Gibbs free energy value and non-reactivity demand higher input of energy for the conversion of CO_2 into valuables.[104] The use of biocatalysts can undoubtedly lower the energy required for this process. Not only the use of microbes makes the process cost-effective, but they also operate under mild environmental conditions making the process environmentally sustainable. However, the sensitivity of microbes towards these synthesised chemicals and the requirement of nutrients can be a challenge when scaling up of MES is concerned.[11] The potential of MES technology is immense as it can also be used to store the excess power generated from renewable sources during non-peak hours into C–C bonds of electro-commodities.[105] This technology is still in the development phase, and numerous parameters need to be optimised before a successful full-scale demonstration is possible.

Future Prospects

With the advent of MES technology, it was established that microbes could accept electrons from the solid electrodes and produce value-added reduced products. However, until now, the various parameters affecting the performance of these systems are not optimised. Also, MES is facing major bottleneck of lesser yield as compared to the traditional processes. Considerable engineering interventions are required to make this technology appropriate for field-scale applications. These include not only the design and fabrication of low-cost setup and electrode materials but also the application of genetic engineering to manipulate biological pathways in microorganisms to favour targeted production of the desired compound efficiently.[92] The electron transfer mechanism is a critical step in the bioelectrochemical pathway of CO_2 reduction. Hence, deciphering the intricate details of the process could be a major step towards the understanding and possible improvements of the MES process.[34] The field-scale applicability of this innovative technology and purity of the products should be targeted.

Operational parameters like catholyte pH, the partial pressure of H_2, electrode potential, etc., greatly affect the performance of MES.[17,20,33] The microbes residing in the cathodic chamber of a MES are only active in a certain pH range, which is close to neutral; however, the type of biocatalysts used also majorly affects this suitable pH range. Furthermore, the catholyte pH also affects the rate of hydrogen production in the cathodic chamber of MES with acidic pH favouring the hydrogen production due to higher availability of protons.[70] Therefore, an optimal pH balancing both these phenomena should be determined, which could aid in the production of a higher quantity of organic compounds through MES.

Similarly, the partial pressure of H_2 also affects the rate of hydrogen production and in turn the performance of MES. Moreover, the externally applied cathodic potential also governs numerous bioelectrochemical reactions taking place in the cathodic chamber. Also, to target the production of a single organic compound, a potential stimulating the reaction leading to the formation of the target compound should be determined and employed in MES. Also, the application of more negative potential can increase the production of organic compounds due to the supply of a higher number of electrons to the microbes.[33] However, with the increase in applied potential, the operating cost increases as there is a cost associated with each unit of electrical energy supplied for MES. This again calls for the optimization of the electrode potential required for effective production of organic chemicals through MES. Therefore, optimising these parameters, which govern the bioelectrochemical reactions taking place in the cathodic chamber of a MES, can be significant step towards improving the productivity of the process.

Moreover, MES can also be used to develop the concept of biorefineries, where excess renewable electrical power can be stored in C-C bonds,[106] which can be utilised later.[77] Thus, the energy lost during the non-peak hours can be successfully recovered and reused in the form of organic compounds. Furthermore, this technology doesn't require arable land for the production of biofuels rendering it free from the debate of food vs fuel.[107] The conversion efficiency of photovoltaic systems ranges from 10% to 15%, and for photosynthesis in plants, it is around 0.5%.[31] If MES is coupled with a photovoltaic system and assuming 30% efficiency of MES, the overall efficiency comes out to be 4.5%, which is nine times higher than the bio-based processes.[13] Hence, it can be anticipated that a nine-fold increment in bioproduction can be achieved when MES is powered using solar power.

In addition, MES is free from the problem of the requirement of a large amount of freshwater and nutrients for the bioproduction of electro-commodities. The use of gaseous waste streams generated from various industries also significantly reduces the cost of raw materials required for the synthesis of chemicals. Thus by using MES, a closed-loop system can be developed, where biorefineries can be integrated with chemical industries for making the overall process sustainable.[85] The technical feasibility of such a concept has been already proved.[97] Along with these encouraging aspects, it is also a cleaner and greener technology and therefore, it can be envisioned as a potential substitute for traditional processes in the near future.

Conclusions

A brief overview of the recent developments in terms of cathode materials and biocatalysts used in MES along with the feasibility of the process, in the long run, are being discussed. The research gaps or challenges and scope for future research pertaining to bioelectrochemical CO_2 sequestration are also focused. The economic feasibility of the process considering the synthesis of various organic compounds is also briefly discussed. Considerable research has been carried out in this field in recent times; however, still substantial investigations on optimization of numerous parameters governing the process performance are required to realize its implementation in the field. After optimizing the performance, this emerging technology of MES could offer a sustainable option to alleviate the ever-increasing environmental problems.

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References

1. M. Parry, O. Canziani, J. Palutikof, P. J. van der Linden, and C. E. Hanson, *Climate change 2007: Impacts, Adaptation and Vulnerability Climate change: Impacts, Adaptation and Vulnerability* (2007), https://www.eea.europa.eu/data-and-maps/indicators/soil-organic-carbon-1/IRationaleReference1232455014617.
2. K. Rabaey and R. A. Rozendal, *Nat. Rev. Microbiol.*, **8**, 706 (2010).
3. I. Das, S. Das, S. Sharma, and M. Ghangrekar, *Int. J. Hydrog. Energy*, **45**, 16787 (2020).
4. S. Das, S. Das, I. Das, and M. Ghangrekar, *Mater. Sci. Energy Technol.*, **2**, 687 (2019).
5. D. Pant, A. Singh, G. Van Bogaert, S. Irving Olsen, P. Singh Nigam, L. Diels, and K. Vanbroekhoven, *RSC Adv.*, **2**, 1248 (2012).
6. P. Majumdar, D. Pant, and S. Patra, *Trends Biotechnol.*, **35**, 285 (2017).
7. S. Das and M. Ghangrekar, *Indian J. Exp. Biol.*, **56**, 470 (2018).
8. L. Jourdin, S. M. Raes, C. J. Buisman, and D. P. Strik, *Front. Energy Res.*, **6**, 7 (2018).
9. P. Batlle-Vilanova, R. Ganigué, S. Ramió-Pujol, L. Baneras, G. Jiménez, M. Hidalgo, M. D. Balaguer, J. Colprim, and S. Puig, *Bioelectrochemistry*, **117**, 57 (2017).
10. K. J. Steinbusch, H. V. Hamelers, C. M. Plugge, and C. J. Buisman, *Energy Environ. Sci.*, **4**, 216 (2011).
11. D. R. Lovley and K. P. Nevin, *Curr. Opin. Biotechnol.*, **24**, 385 (2013).
12. T.-s. Song, H. Zhang, H. Liu, D. Zhang, H. Wang, Y. Yang, H. Yuan, and J. Xie, *Bioresour. Technol.*, **243**, 573 (2017).
13. S. Bajracharya, K. Vanbroekhoven, C. Buisman, D. Strik, and P. Deepak, *Faraday Discuss.*, **202**, 433 (2017).
14. P. Batlle-Vilanova, S. Puig, R. Gonzalez-Olmos, M. D. Balaguer, and J. Colprim, *J. Chem. Technol. Biotechnol.*, **91**, 921 (2016).
15. K. P. Nevin, T. L. Woodard, A. E. Franks, Z. M. Summers, and D. R. Lovley, *mBio*, **1**, e00103-00110 (2010).
16. B. Bian, S. Bajracharya, J. Xu, D. Pant, and P. E. Saikaly, *Bioresour. Technol.*, **302**, 122863 (2020).
17. G. Mohanakrishna, K. Vanbroekhoven, and D. Pant, *J. CO2 Util.*, **15**, 57 (2016).
18. S. Srikanth, Y. Alvarez-Gallego, K. Vanbroekhoven, and D. Pant, *Chem. Phys. Chem*, **18**, 3174 (2017).
19. P.-L. Tremblay and T. Zhang, *Front. Microbiol.*, **6**, 201 (2015).
20. D. R. Bond and D. R. Lovley, *Appl. Environ. Microbiol.*, **69**, 1548 (2003).
21. Y. Wu, F. Li, T. Liu, R. Han, and X. Luo, *Electrochim. Acta*, **213**, 408 (2016).
22. B. Huang, G. Fu, C. He, H. He, C. Yu, and X. Pan, *J. Electroanal. Chem.*, **851**, 113464 (2019).
23. S. B. Velasquez-Orta, I. M. Head, T. P. Curtis, K. Scott, J. R. Lloyd, and H. von Canstein, *Appl. Microbiol. Biotechnol.*, **85**, 1373 (2010).
24. H.-B. Shen, X.-Y. Yong, Y.-L. Chen, Z.-H. Liao, R.-W. Si, J. Zhou, S.-Y. Wang, Y.-C. Yong, P.-K. OuYang, and T. Zheng, *Bioresour. Technol.*, **167**, 490 (2014).
25. M. Rahimnejad, G. D. Najafpour, A. A. Ghoreyshi, F. Talebnia, G. C. Premier, G. Bakeri, J. R. Kim, and S.-E. Oh, *J Microbiol*, **50**, 575 (2012).
26. S. Bajracharya, K. Vanbroekhoven, C. J. Buisman, D. Pant, and D. P. Strik, *Environ. Sci. Pollut. Res.*, **23**, 22292 (2016).
27. D. Park, M. Laivenieks, M. Guettler, M. Jain, and J. Zeikus, *Appl. Environ. Microbiol.*, **65**, 2912 (1999).
28. M. J. J. Mayer, C. J. N. Buisman, H. V. M. Hamelers, and D. P. B. T. B. Strik, "Device and method for performing a biologically catalyzed electrochemical reaction." *United States Patent*, US9105913B2 (2015).
29. E. Marsili, D. B. Baron, I. D. Shikhare, D. Coursolle, J. A. Gralnick, and D. R. Bond, *Proc. Natl. Acad. Sci. U. S. A.*, **105**, 3968 (2008).
30. T. D. Harrington, A. Mohamed, V. N. Tran, S. Biria, M. Gargouri, J.-J. Park, D. R. Gang, and H. Beyenal, *Bioresour. Technol.*, **195**, 57 (2015).
31. K. Rabaey, P. Girguis, and L. K. Nielsen, *Curr. Opin. Biotechnol.*, **22**, 371 (2011).
32. N. Aryal, F. Ammam, S. A. Patil, and D. Pant, *Green Chem.*, **19**, 5748 (2017).
33. S. Das, I. Das, and M. Ghangrekar, *J. Environ. Chem. Eng.*, **8**, 104028 (2020).
34. D. R. Lovley, *Environ. Microbiol. Rep.*, **3**, 27 (2011).
35. Z. Zaybak, J. M. Pisciotta, J. C. Tokash, and B. E. Logan, *J. Biotechnol.*, **168**, 478 (2013).
36. T. Zhang, H. Nie, T. S. Bain, H. Lu, M. Cui, O. L. Snoeyenbos-West, A. E. Franks, K. P. Nevin, T. P. Russell, and D. R. Lovley, *Energy Environ. Sci.*, **6**, 217 (2013).
37. J. A. Modestra, B. Navaneeth, and S. V. Mohan, *J. CO2 Util.*, **10**, 78 (2015).
38. A. Ghorai, S. Roy, S. Das, H. Komber, M. M. Ghangrekar, B. Voit, and S. Banerjee, *ACS Applied Polymer Materials*, **2**, 2967 (2020).
39. S. Bajracharya, S. Srikanth, G. Mohanakrishna, R. Zacharia, D. P. Strik, and D. Pant, *J. Power Sources*, **356**, 256 (2017).
40. S. Das, I. Chakraborty, P. Rajesh, and M. Ghangrekar, *J. Hazard. Toxic Radioact. Waste*, **24**, 04020009 (2020).
41. S. Cheng, D. Xing, D. F. Call, and B. E. Logan, *Environ. Sci. Technol.*, **43**, 3953 (2009).
42. P.-L. Tremblay, D. Höglund, A. Koza, I. Bonde, and T. Zhang, *Sci. Rep.*, **5**, 16168 (2015).
43. K. P. Nevin, S. A. Hensley, A. E. Franks, Z. M. Summers, J. Ou, T. L. Woodard, O. L. Snoeyenbos-West, and D. R. Lovley, *Appl. Environ. Microbiol.*, **77**, 2882 (2011).
44. J. Arends, *Optimizing the plant microbial fuel cell: Diversifying applications and product outputs*, Ghent University (2013).
45. S. Bajracharya, A. ter Heijne, X. Dominguez Benetton, K. Vanbroekhoven, C. J. Buisman, D. P. Strik, and D. Pant, *Bioresour. Technol.*, **195**, 14 (2015).
46. N. Aryal, P.-L. Tremblay, D. M. Lizak, and T. Zhang, *Bioresour. Technol.*, **233**, 184 (2017).
47. E. Blanchet, F. Duquenne, Y. Rafrafi, L. Etcheverry, B. Erable, and A. Bergel, *Energy Environ. Sci.*, **8**, 3731 (2015).
48. E. V. LaBelle, C. W. Marshall, J. A. Gilbert, and H. D. May, *PLoS One*, **9**, e109935 (2014).
49. Y. Jiang, M. Su, Y. Zhang, G. Zhan, Y. Tao, and D. Li, *Int. J. Hydrog. Energy*, **38**, 3497 (2013).
50. S. A. Patil, J. B. Arends, I. Vanwonterghem, J. Van Meerbergen, K. Guo, G. W. Tyson, and K. Rabaey, *Environ. Sci. Technol.*, **49**, 8833 (2015).
51. S. Das, P. Chatterjee, and M. Ghangrekar, *Water Sci. Technol.*, **77**, 1293 (2018).
52. I. Das, S. Das, and M. Ghangrekar, *Chem. Phys. Lett.*, **751**, 137536 (2020).
53. P. Chiranjeevi and S. A. Patil, *Biotechnol. Adv.*, **39**, 107468 (2020).
54. C. W. Marshall, D. E. Ross, E. B. Fichot, R. S. Norman, and H. D. May, *Environ. Sci. Technol.*, **47**, 6023 (2013).
55. T. Ueki, K. P. Nevin, T. L. Woodard, and D. R. Lovley, *mBio*, **5**, e01636 (2014).
56. H. L. Drake, A. S. Gößner, and S. L. Daniel, *Annals NY Academy of Sciences*, **1125**, 100 (2008).
57. K. Igarashi and S. Kato, *Appl. Microbiol. Biotechnol.*, **101**, 6301 (2017).
58. R. Ganigué, S. Puig, P. Batlle-Vilanova, M. D. Balaguer, and J. Colprim, *Chem. Commun.*, **51**, 3235 (2015).
59. J. Phillips, K. Klasson, E. Clausen, and J. Gaddy, *Appl. Biochem. Biotechnol.*, **39**, 559 (1993).
60. L. Soussan, J. Riess, B. Erable, M.-L. Délia, and A. Bergel, *Electrochem. Commun.*, **28**, 27 (2013).
61. S. Srikanth, D. Singh, K. Vanbroekhoven, D. Pant, M. Kumar, S. Puri, and S. Ramakumar, *Bioresour. Technol.*, **265**, 45 (2018).
62. S. Bajracharya, B. van den Burg, K. Vanbroekhoven, H. De Wever, C. J. N. Buisman, D. Pant, and D. P. B. T. B. Strik, *Electrochim. Acta*, **237**, 267 (2017).
63. S. Gildemyn, K. Verbeeck, R. Jansen, and K. Rabaey, *Bioresour. Technol.*, **224**, 358 (2017).
64. T. s. Song, K. Fei, H. Zhang, H. Yuan, Y. Yang, P. Ouyang, and J. Xie, *J. Chem. Technol. Biotechnol.*, **93**, 457 (2018).
65. A. Gupta, S. Das, and M. Ghangrekar, *Chem. Phys. Lett.*, **754**, 137690 (2020).
66. L. Chen, P.-L. Tremblay, S. Mohanty, K. Xu, and T. Zhang, *J. Mater. Chem. A*, **4**, 8395 (2016).
67. S. Das, A. Mishra, and M. Ghangrekar, *J. Hazard. Toxic Radioact. Waste*, **24**, 06020001 (2020).
68. N. Faraghiparapari and K. Zengler, *J. Chem. Technol. Biotechnol.*, **92**, 375 (2017).
69. J. B. Arends, S. A. Patil, H. Roume, and K. Rabaey, *J. CO2 Util.*, **20**, 141 (2017).
70. L. Jourdin, Y. Lu, V. Flexer, J. Keller, and S. Freguia, *Chem. Electro. Chem*, **3**, 581 (2016).
71. E. V. LaBelle and H. D. May, *Front. Microbiol.*, **8**, 756 (2017).
72. M. Kuroda and T. Watanabe, *Energy Convers. Manage.*, **36**, 787 (1995).
73. N. Aryal, A. Halder, M. Zhang, P. R. Whelan, P.-L. Tremblay, Q. Chi, and T. Zhang, *Sci. Rep.*, **7**, 1 (2017).
74. L. Jourdin, S. Freguia, B. C. Donose, J. Chen, G. G. Wallace, J. Keller, and V. Flexer, *J. Mater. Chem. A*, **2**, 13093 (2014).
75. L. Jourdin, S. Freguia, V. Flexer, and J. Keller, *Environ. Sci. Technol.*, **50**, 1982 (2016).
76. L. Jourdin, T. Grieger, J. Monetti, V. Flexer, S. Freguia, Y. Lu, J. Chen, M. Romano, G. G. Wallace, and J. Keller, *Environ. Sci. Technol.*, **49**, 13566 (2015).
77. M. D. P. A. Rojas et al., *Energy Convers. Manage.*, **177**, 272 (2018).
78. K. Verbeeck, S. Gildemyn, and K. Rabaey, *Front. Energy Res.*, **6**, 88 (2018).
79. C. W. Marshall, D. E. Ross, E. B. Fichot, R. S. Norman, and H. D. May, *Appl. Environ. Microbiol.*, **78**, 8412 (2012).
80. B. Avasarala, R. Moore, and P. Haldar, *Electrochim. Acta*, **55**, 4765 (2010).
81. M. Sára and U. B. Sleytr, *J. Bacteriol.*, **182**, 859 (2000).
82. H. Nie, T. Zhang, M. Cui, H. Lu, D. R. Lovley, and T. P. Russell, *Phys. Chem. Chem. Phys.*, **15**, 14290 (2013).
83. S. Bajracharya, A. ter Heijne, X. D. Benetton, K. Vanbroekhoven, C. J. Buisman, D. P. Strik, and D. Pant, *Bioresour. Technol.*, **195**, 14 (2015).
84. M. Cui, H. Nie, T. Zhang, D. Lovley, and T. P. Russell, *Sustain. Energy Fuels*, **1**, 1171 (2017).
85. A. ElMekawy, H. M. Hegab, D. Losic, C. P. Saint, and D. Pant, *Renew. Sustain. Energy Rev.*, **72**, 1389 (2017).
86. N. Aryal, A. Halder, P.-L. Tremblay, Q. Chi, and T. Zhang, *Electrochim. Acta*, **217**, 117 (2016).
87. M. Zhou, Q. Weng, Z. I. Popov, Y. Yang, L. Y. Antipina, P. B. Sorokin, X. Wang, Y. Bando, and D. Golberg, *ACS nano*, **12**, 4148 (2018).
88. N. Lotfi, T. Shahrabi, Y. Yaghoubinezhad, and G. B. Darband, *Electrochim. Acta*, **326**, 134949 (2019).
89. S. Badrayyana, D. K. Bhat, S. Shenoy, Y. Ullal, and A. C. Hegde, *Int. J. Hydrog. Energy*, **40**, 10453 (2015).
90. L. Yang, W. Zhou, J. Jia, T. Xiong, K. Zhou, C. Feng, J. Zhou, Z. Tang, and S. Chen, *Carbon*, **122**, 710 (2017).
91. S. Ahmad, A. Sadhanala, R. L. Hoye, V. Andrei, M. H. Modarres, B. Zhao, J. Rongé, R. Friend, and M. D. Volder, *ACS Applied Materials & Interfaces*, **11**, 23198 (2019).
92. C. G. Giddings, K. P. Nevin, T. Woodward, D. R. Lovley, and C. S. Butler, *Front. Microbiol.*, **6**, 468 (2015).

93. A. ElMekawy, H. M. Hegab, G. Mohanakrishna, A. F. Elbaz, M. Bulut, and D. Pant, *Bioresour. Technol.*, **215**, 357 (2016).
94. J. A. Lara-Gil, M. M. Álvarez, and A. Pacheco, *J. Appl. Phycol.*, **26**, 357 (2014).
95. S. Gildemyn, K. Verbeeck, R. Slabbinck, S. J. Andersen, A. Prévoteau, and K. Rabaey, *Environ. Sci. Technol. Lett.*, **2**, 325 (2015).
96. C. Leang, T. Ueki, K. P. Nevin, and D. R. Lovley, *Appl. Environ. Microbiol.*, **79**, 1102 (2013).
97. X. Christodoulou and S. B. Velasquez-Orta, *Environ. Sci. Technol.*, **50**, 11234 (2016).
98. P. Pal and J. Nayak, *Sep. Purif. Rev.*, **46**, 44 (2017).
99. J. W. Lee, *Advanced Biofuels and Bioproducts* (Springer Science & Business Media, Norfolk, USA) (2012).
100. S. S. Yazdani and R. Gonzalez, *Curr. Opin. Biotechnol.*, **18**, 213 (2007).
101. J. H. Sim, A. H. Kamaruddin, W. S. Long, and G. Najafpour, *Enzyme Microb. Technol.*, **40**, 1234 (2007).
102. C.-H. Huang and C.-S. Tan, *Aerosol Air Qualilty Res.*, **14**, 480 (2014).
103. K. P. Katuri, S. Kalathil, A. A. Ragab, B. Bian, M. F. Alqahtani, D. Pant, and P. E. Saikaly, *Adv. Mater.*, **30**, 1707072 (2018).
104. S. Roy, A. Schievano, and D. Pant, *Bioresour. Technol.*, **213**, 129 (2016).
105. M. D. P. A. Rojas, M. Zaiat, E. R. Gonzalez, H. D. Wever, and D. Pant, *Bioresour. Technol.*, **266**, 203 (2018).
106. J. Sadhukhan, J. R. Lloyd, K. Scott, G. C. Premier, H. Y. Eileen, T. Curtis, and I. M. Head, *Renew. Sustain. Energy Rev.*, **56**, 116 (2016).
107. J. Desloover, J. B. Arends, T. Hennebel, and K. Rabaey, *Biochem. Soc. Trans.*, **40**, 1233 (2012).