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Review

Microbial electrolysis cells turning to be versatile technology: Recent advances and future challenges

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ABSTRACT

Microbial electrolysis cells (MECs) are an electricity-mediated microbial bioelectrochemical technology, which is originally developed for high-efficiency biological hydrogen production from waste streams. Compared to traditional biological technologies, MECs can overcome thermodynamic limitations and achieve high-yield hydrogen production from wide range of organic matters at relatively mild conditions. This approach greatly reduces the electric energy cost for hydrogen production in contrast to direct water electrolysis. In addition to hydrogen production, MECs may also support several energetically unfavorable biological/chemical reactions. This unique advantage of MECs has led to several alternative applications such as chemicals synthesis, recalcitrant pollutants removal, resources recovery, bioelectrochemical research platform and biosensors, which have greatly broaden the application scopes of MECs. MECs are becoming a versatile platform technology and offer a new solution for emerging environmental issues related to waste streams treatment and energy and resource recovery. Different from previous reviews that mainly focus on hydrogen production, this paper provides an up-to-date review of all the new applications of MECs and their resulting performance, current challenges and prospects of future.

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1. Introduction

The use of fossil fuels in recent years has accelerated the depletion of non-renewable resources. Furthermore, the unprecedented increase in greenhouse gas emissions due to combustion of fossil fuels causes global warming and climate change. A sustainable and carbon-neutral energy source as alternatives to fossil fuels is highly needed to alleviate the global energy crisis and climate change. Bioenergy technologies which use renewable resources such as wastewater to produce biofuels or valuable chemicals will play a role.

Bioelectrochemical systems (BESs) as a young generation of bioenergy technology possesses a tremendous potential for simultaneous wastewater treatment and electric energy generation or valuable chemicals production (Chaudhuri and Lovley, 2003; Aelterman et al., 2006; Jacobson et al., 2011; Logan et al., 2006; Lovley and P.E, 1988; Zhang and Angelidaki, 2012a, 2013). There are two types of BESs according to the way of using electricity. One is known as microbial fuel cells (MFCs) which produce electricity from organic waste streams, while another is known as microbial electrolysis cells (MECs) which require electricity supply for hydrogen production from organic waste streams (Logan et al., 2006; Kundu et al., 2013). MFCs as one of typical BESs have attracted extensive attentions at the early stage of BESs research (Cheng et al., 2006; He and Mansfeld, 2009; Liu et al., 2005a; Logan, 2005; Rabaey et al., 2005; Zhang et al., 2011). While interesting, researchers are realizing that the economic and environmental value of electricity from MFCs cannot compete with that of other energy sources (e.g., biogas) at this stage. Therefore, a development has been recently initiated to broad the scope of MFCs for more value-added applications, such as hydrogen production by MECs (Fig. 1). The concept of MECs was proposed by two groups almost at the same period (Liu et al., 2005b; Rozendal et al., 2006). This technology was firstly nominated as "electrochemically assisted hydrogen generation", then "biocatalyzed electrolysis", "electrohydrogenesis", and was finally accepted by researchers as "microbial electrolysis cells (MECs)" (Liu et al., 2005b; Cheng and Logan, 2007; Logan et al., 2008; Rozendal et al., 2007; Zhang and Angelidaki, 2012b). MECs have several advantages over other biological hydrogen production processes. Various organic matters such as cellulose, glucose, glycerol, acetic acid, sewage sludge and varied wastewaters can be converted to hydrogen in MECs (Liu et al., 2005b; Cheng and Logan, 2007; Logan et al., 2008; Pant et al., 2012). MECs can even convert the byproducts of dark fermentation (e.g., acetate) into hydrogen with high H_2 yields (e.g., 12 mol-H_2/mol-glucose in theory) (Liu et al., 2005b; Logan et al., 2008). Furthermore, MECs require relatively low energy input (0.2–0.8 V) compared to typical water electrolysis (>2.1 V).

Over the past decade, MECs as a promising platform for H_2 production and alternative applications have drawn much more attention in scientific communities, resulting in rapid advances in the field and extensive journal publications. Fig. 2A shows that the number of publications increased sharply and over 284 articles have been published until January 2013. Furthermore, researchers are distributed in different countries showing that MECs have attracted global attention (Fig. 2B). Similar to the development of MFCs, the

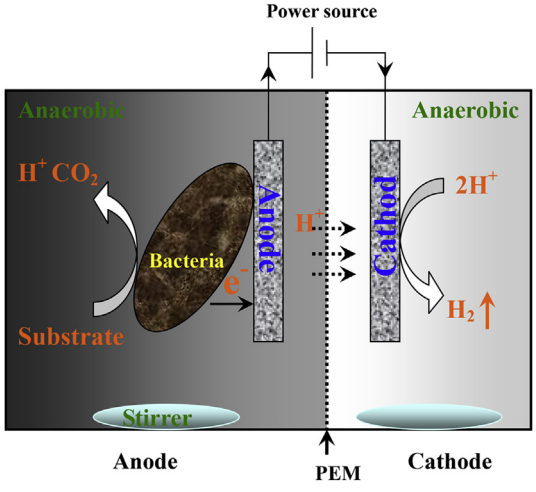

Fig. 1 – Schematic diagram of typical two-chamber MECs for hydrogen production.

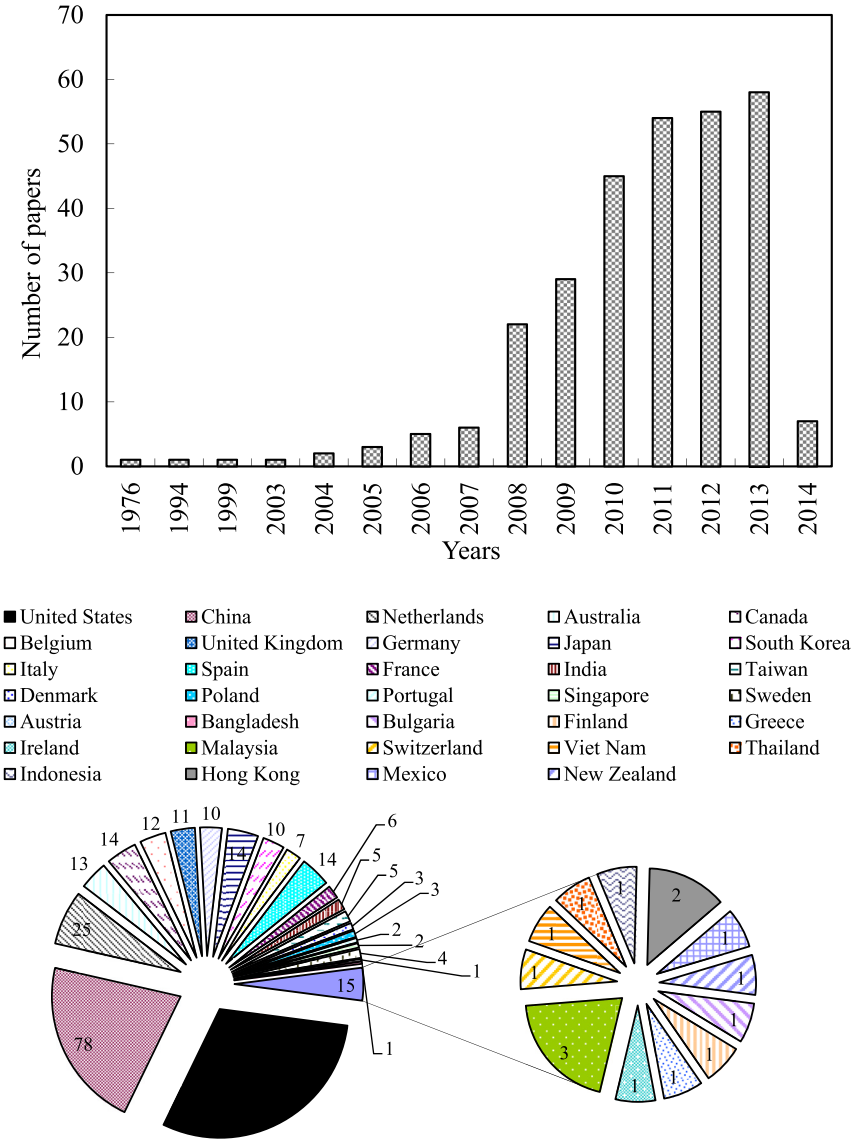

Fig. 2 – The number of journal papers on MECs (A) and the country-wise distribution of articles on MECs (B). The number of articles is based on "Scopus" search using "microbial electrolysis cell" as keyword in January 2014.

research interest of MECs in the early stage lies in onefold direction i.e. H_2 production. Contrary to a mass of research papers, only a few review articles are available. In the first state of the art review on MECs, the reactor architectures, materials, system performance, energy efficiencies and challenges for hydrogen production were reviewed, which offers an insight to the later MECs research works (Logan et al., 2008). Geelhoed et al. (2010) further reviewed the foundation knowledge, technological design concepts and electron transfer mechanisms of electricity-driven hydrogen production. Lee et al. (2010) compared different biological hydrogen production technologies and highlighted the foundation, advantages and challenges of MECs for hydrogen production. More recently, Sleutels et al. (2012) briefly addressed the essential factors affecting the practical application of MECs from the economic point of view. Kundu et al. (2013) summarized the recent efforts on the development of cost-effective cathodes or cathode catalysts for hydrogen generation. These articles indeed provide overview of the MECs with different favor or emphasis. However, these reviews mainly focus on the function of MECs for hydrogen production. The emerging alternative applications of MECs for recalcitrant pollutants removal, resources recovery, chemicals synthesis, bioelectrochemical research platform and biosensor have not yet been reviewed. Therefore, this paper provides a comprehensive review of all the different application possibilities developed so far from the MECs platform. The scientific and technical challenges in the future with respect to different applications are also discussed.

2. Power supply: a driving-force of MEC-based applications

External electricity supply is the driving force of MECs for different applications, which also distinguishes MECs from

other BESs. Although the voltage level required by MECs is much lower than that of water electrolysis process (1.8–2.0 V), the energy consumption is still high, especially for long-term operation in rural or remote area where electricity distribution is difficult to reach. Therefore, reduction of electric energy costs or development of alternative renewable power sources is essential to the successful application of MECs. Table 1 shows the reported alternative power sources to DC power supply or potentiostat. In Section 2.3, alternative ways of power supply that have not been experimentally demonstrated but have potential if proper application niches are identified are discussed.

2.1. MFCs power

MFCs are one of typical BESs capable of electricity production from wastewater and thus are deemed as a potential renewable power source. The voltage produced by MFCs is generally around 0.8 V, which is theoretically sufficient to support the electric energy required by MECs. Sun et al. (2008) demonstrated the possibility of using a single chamber MFC to directly power a two-chamber MEC. They also found that the input voltage of the MEC can be adjusted by external resistance in a series circuit (Sun et al., 2010). In order to improve the voltage supply, one or two additional MFCs were introduced into the MFC-MEC coupled system (Sun et al., 2009). The hydrogen production was significantly enhanced by connecting MFCs in series, while opposite results was observed with parallel connection. Therefore, connecting several MFCs in series could be an efficient way to improve the voltage supply in such coupled system. MFCs have also been used to power CO_2 reduction in the cathode of MECs, which further shows the promising perspective of MFCs as power sources of MECs (Zhao et al., 2012a).

Nevertheless, there are several challenges need to be addressed before field application. For example, the voltage supplied to the MECs is still low compared to the maximum value observed in typical MECs studies (around 0.8 V) (Cheng and Logan, 2007). The input voltage of MECs could be improved by connecting several MFCs in series, but this method may not be feasible for long-term operation due to voltage reversal (Oh and Logan, 2007; Zhang and Angelidaki, 2012c). Another key limitation could be the interaction of these two systems (i.e. MFCs and MECs), which make the system unstable and lead to the deterioration of performance. To avoid aforementioned limitations, a novel method was proposed recently to boost voltage output and electricity transfer efficiency of MFCs by using a capacitor in the circuit (Hatzell et al., 2013). MFCs were connected in parallel to charge capacitors, and then the capacitors were discharged in series to boost the output voltage supplied to MECs. With such system, energy recoveries were improved from 9 to 13% and hydrogen production increased from 0.31 to 0.72 m^3/m^3/day.

2.2. Solar power

Among renewable energy sources, solar energy due to its huge amount and availability is considered to be one of the most viable choices to meet energy demand worldwide. Therefore, solar power could be an efficient and sustainable power source for MECs. Dye sensitized solar cell (DSSC) has been used to provide an additional reductive power from light to an MEC (Ajayi et al., 2009). The coupled system was tested for hydrogen production. An open circuit voltage of 0.6 V was produced by the DSSC and then supplied to the MEC. The whole system produced 400 μmol H_2 within 5 h with cathode recovery efficiency of 78%. In order to further reduce the cost of this coupled system, the platinum catalyst-free cathode of MEC was developed (Chae et al., 2009). The system with plain cathode produced almost the same level of hydrogen as that produced with Pt-loaded carbon felt electrodes when voltage was higher than 0.7 V. Furthermore, significantly enhancement in hydrogen production was observed using carbon nanopowder-coated electrode without Pt (Chae et al., 2009). Through solar cell-MEC-coupled system, solar energy is converted to liquid or gas transportation fuels (i.e., hydrogen, methane, and ethanol) which can be stored for future use. To further improve the system performance, connecting several solar cells in series is needed in future work.

2.3. Unexplored alternative ways of power supply

Beside aforementioned power sources, several renewable electricity sources (e.g., wind, waste heat, geothermal, and ocean power) could be alternative ways of power supply for MECs. Wind power as the fastest growing electricity

Table 1 – Alternative powers source for MECs.

Power source	MEC reactor	Substrate of MEC	Input voltage (V)	Current (A/m^2)	Maximum H_2 production rate (m^3/m^3/day)	Reference
Single chamber MFC	Two-chamber MEC	Acetate	0.348	0.404	0.0149	(Sun et al., 2008)
Single chamber MFC	Two-chamber MEC	Propionate	0.274	0.343	0.0119	(Sun et al., 2010)
MFC stack	Two-chamber MEC	Acetate	0.364–0.807	0.078–0.418	0.0145	(Sun et al., 2009)
MFC stack with capacitor	Cube-shaped, single-chamber	Acetate	0.48	–[a]	0.72	(Hatzell et al., 2013)
Dye sensitized solar cell	Dual chambered MEC	Acetate	0.602	1.5	0.14[b]	(Ajayi et al., 2009)
Dye sensitized solar cell	H-shaped two-chambered	Acetate	0.7	1.0[b]	0.07	(Chae et al., 2009)
Dye sensitized solar cell	Two-chambered	Acetate	0.707	2.6	0.5[b]	(Ajayi et al., 2010)

[a] Not stated.
[b] Estimated number based on the available data.

generation source has gained much attention over the past years, wind farms are being installed in many countries (e.g., Denmark) for additional electricity generation (Purvins et al., 2011). Wind turbines can be either hundreds meters tall for on-shore or off-shore area or a few meters small for home or remote locations. Compared to conventional power plants, the installation of wind turbines/mills is faster. Considering the above, wind power could be easily integrated with MECs regardless of regional restriction, e.g., in remote areas.

Waste heat is generally produced by machines or other processes that use energy (Gewald et al., 2012). Recovery of waste heat from industrial processes will bring both environmental and economic benefits. However, few methods are available to capture waste heat energy at low temperatures. It has been recently reported that waste heat can be converted to electricity in a BES termed microbial reverse-electrodialysis cells (MREC) using a heat-regenerated ammonia bicarbonate salt solution (Cusick et al., 2012). The system produced a maximum power density of 5.6 W/m^2. Therefore, the electricity produced by MREC from waste heat could be a power source for MECs. It was subsequently found that hydrogen could be produced at the cathode of such system using several pairs of membranes (Nam et al., 2012). In this case, the MREC is function as an MEC, but the only difference is that the process in MREC is powered by waste heat and no external electricity supply is required. In the view of energy consumption, MREC could be an promising and alternative platform to typical MEC for other applications than hydrogen production (e.g., chemical production discussed in following sections). Geothermal power, hydropower and ocean power could also be alternative electricity sources to MECs.

Linking MECs with aforementioned renewable energy sources offers a connection between renewable electricity production and transportation, stationary and portable energy needs. The electricity from wind, waste heat, geothermal, ocean and hydro is fully utilized only during high load periods, and is wasted in low load periods. The excess electricity could be delivered to MECs e.g., for chemical production. In this case, the excess electric energy are stored as liquid or gas transportable fuels (e.g., H_2, ethanol) to meet a variety of needs. Nevertheless, all these hypothesis need to be studied in future.

3. The diverse application possibility of MECs platform

3.1. *Microbial electrosynthesis of chemicals*

3.1.1. *Methane*

Methane is commonly detected in the MECs during hydrogen production due to the growth of methanogens. The methane production from MECs is varied with inoculum, substrate and reactor configuration (Chae et al., 2010). The appearance of methanogens is unexpected in hydrogen-producing MECs, as it lowers the hydrogen production. Several approaches have been employed to inhibit the growth of methanogens in MECs (Call and Logan, 2008; Clauwaert and Verstraete, 2009; Wang et al., 2009). However, most of the methods are ineffective or energy intensive. Instead of inhibition of methanogens, direct production of methane in MECs holds several advantages compared to traditional anaerobic digestion processes. Firstly, organic matter oxidation and methane production are two separated processes in MECs which allow high methane content in biogas. Secondly, the process occurs at ambient temperature, i.e. heating is not required, thereby saving energy. Thirdly, methanogens can accept electrons directly from cathode, which may make the process more tolerant to toxic compounds such as ammonia (Clauwaert et al., 2008). Fourthly, MECs can use waste streams with low organic matter content, where anaerobic digestion cannot function (Villano et al., 2011). At the early stage, methane production in the cathode of MECs was mediated by hydrogen with abiotic cathode. Clauwaert et al. (2008) found that hydrogen produced from the cathode of MECs can be further converted to methane in an external anaerobic digester, where the process was not inhibited even at ammonium concentration of 5 g-N/L. The application of biocathode has greatly reduced the costs of electrode catalyst in MECs. In a two-chamber MEC with biocathode, methane production rate reached to 0.06 mmol/L/h at voltage of 1.2 V (Table 2) (Cheng et al., 2009). MECs can be an alternative and promising technology to store electrical energy generated from renewable energy sources such as wind and solar into biofuels as well as contribute to CO_2 mitigation. However, MECs will not likely to replace conventional anaerobic

Table 2 – Summary of the products from MECs platform.

Products	MEC reactor	Electron acceptor[a]	Cathode	Voltage added (V)	Production rate (mmol/L/h)[b]	References
Methane (CH_4)	Single/two-chamber	CO_2	Biocathode	0.7–1.0	0.06	(Cheng et al., 2009)
Ethanol (C_2H_6O)	Two-chamber	Acetate	Biocathode	−0.55[d]	0.00003	(Steinbusch et al., 2010)
Formic acid (CH_2O_2)	Two-chamber	CO_2	Pb	1.13[c]	0.09	(Zhao et al., 2012b)
Hydrogen peroxide (H_2O_2)	Two-chamber	O_2	Carbon cloth gas diffusionelectrode	0.5	1.17	(Rozendal et al., 2009)
Acetate ($C_2H_3O_2^-$)	Two-chamber	CO_2	Graphite sticks	0.4	–[e]	(Nevin et al., 2010)

[a] Electron acceptor in the cathode chamber.
[b] Calculated based on total reactor volume with the available data.
[c] The power source is MFC stack.
[d] Cathode potential.
[e] Not provided.

digestion processes, as MECs are more favorable for low-strength waste streams. Therefore, MECs can be a complement of anaerobic digestion e.g., as downstream process to polish anaerobic digestion effluent.

3.1.2. *Ethanol*

Recently, the feasibility of ethanol production by using electrode instead of hydrogen as electron donor in a biocathode MEC has been demonstrated (Table 2) (Steinbusch et al., 2010). In a two-chamber MEC, acetate was reduced to ethanol via the assistance of electron mediator such as methyl viologen (MV). When the cathode potential was set at −0.55 V, a maximum current density of 1.33 A/m^2 was obtained after MV addition, leading to 1.82 mM ethanol production. The ethanol production was mainly dependent on the MV concentrations, and the production stopped after 5 days when MV was depleted (Steinbusch et al., 2010). MECs platform provide a new way to overcome the limitation of traditional biological ethanol production. However, there are underlying challenges that need to be addressed. The mechanism of acetate reduction in the cathode is still unknown. Since hydrogen (0.0035 $Nm^3/m^2/d$) was observed in the cathode, it could also be involved in acetate reduction. In addition, requirement of irreversibly electron acceptors will add the operation cost, which is a critical challenge for the practical application. Selection of electroactive microorganisms which can accept electrons directly from cathode rather than via mediator for ethanol production could be interesting in future work. In addition to above, the ethanol production rate and the final concentration achieved in the reported system are still low, which will require extensive energy for distillation. Further reduction in electrode overpotential, system internal resistance and energy losses could boost the ethanol production and make the technology industrial applicable.

3.1.3. *Formic acid*

The production of formic acid, which is an important chemical used in pharmaceutical syntheses as well as in paper and pulp production, was achieved based on organic matter oxidation in the anode and CO_2 reduction in the cathode (Table 2) (Zhao et al., 2012b). The electricity required for this process was supplied by a five series-connected MFCs units, which produced an open circuit voltage of 2.73 V. Consequently, formic acid was produced at a rate of 0.09 mM/L/h, and a coulombic efficiency of 64.8% was achieved (Zhao et al., 2012b). This technology will contribute to recover and recycle of the carbon dioxide released during wastewater or waste treatment without energy input, thereby promoting the greenhouse gas reduction. However, the production rate and the final obtained concentration of formic acid are still low at the current stage. The mass transfer and the cathode electrode are two most important factors to the conversion rate. Strategies such as gas diffusion through hollow fiber membrane could be adapted in future work to increase the dissolution of CO_2, and thereby promoting the mass transfer. In addition, the advances in the electrode materials of MFCs such as nanofabrication of electrode surface could also bring benefit to lower the cathode overpotential in MECs.

3.1.4. *Hydrogen peroxide*

Hydrogen peroxide as an important industrial chemical can also be produced by MECs. The feasibility of H_2O_2 production, based on the microbial oxidation of organic matter in the anode coupled to oxygen reduction in the cathode of MECs, has been recently demonstrated (Table 2) (Rozendal et al., 2009). With an external voltage of 0.5 V, this system was capable of producing H_2O_2 at a rate of 1.17 mmol/L/h in the aerated cathode, resulting in an overall efficiency of 83% based on acetate oxidation (Rozendal et al., 2009). Compared to conventional electrochemical method, the H_2O_2 production in MECs requires much lower energy, which was 0.93 kWh/kg-H_2O_2 in the reported study. In principle, H_2O_2 can be produced in MFCs with simultaneous electricity production, which has been demonstrated by several studies (Fu et al., 2010a; You et al., 2010). However, the production rate of H_2O_2 in MFCs was much lower than that of MECs. H_2O_2 production has greatly expanded the application possibilities of MECs. The most attractive application is the combination of Fenton-reaction with MECs, as the MECs can serve as the relatively cheap H_2O_2 source for the Fenton-reaction (Fu et al., 2010b; Zhuang et al., 2010). To become a mature technology, more efforts should be put on the improvement of H_2O_2 concentration. H_2O_2 concentration that can be achieved in MECs at present is only 0.13 wt% (Rozendal et al., 2009), which is still an order of magnitude lower than the expected level for practical industrial implications.

3.1.5. *Acetate*

Solar and wind as renewable sources of energy have gained tremendous attention in the past decade. However, the intermittent nature of these energy sources demands efficient storage technologies to store the unutilized electrical energy. Capture of electric energy in covalent chemical bonds is the first choice, since compounds can be readily stored and supplied on demand via existing infrastructures. Nevin et al. (2010) demonstrated the possibility of reduction of carbon dioxide to acetate by acetogenic microorganism *Sporomusa ovata* with electrons delivered directly from a graphite electrode (Table 2). It was found that *S. ovata* biofilms on the graphite cathode surfaces consumed electrons from electrode and converted carbon dioxide to acetate and small amounts of 2-oxobutyrate. 85% of supplied electrons were captured into these products (Nevin et al., 2010). It is for the first time that the concept of microbial electrosynthesis has been proposed, which provides a highly attractive and novel route that might convert solar energy to valuable organic products more effectively than traditional approaches. As an entire new technology, the related mechanisms, foundation theory and process understanding are still on the way. Rabaey and Rozendal (2010) elucidated the principles, challenges and opportunities of microbial electrosynthesis, gave important point of view on this exciting and new discipline at the nexus of microbiology and electrochemistry.

3.2. *Recalcitrant pollutants removal*

With electricity supply, the cathode potential of MECs can be controlled, and thus recalcitrant pollutants such as

nitrobenzene and 4-chlorophenol in addition to H^+ can be reduced as electron acceptors at cathode (Wang et al., 2012; Wen et al., 2012). Compared to conventional electrochemical reduction, the removal of these pollutants in MECs consumes much less energy. Furthermore, electroactive microorganisms as the catalysts on the anode or cathode of MECs could greatly lower the overpotential of electrochemical reactions, and lead to higher removal efficiencies/rates. Thus, as another application possibility, MECs have been applied for recalcitrant contaminants removal. Table 3 summarized the pollutants which have been treated in MECs so far.

3.2.1. *Organic pollutants*

Generally, most of the organic pollutants such as nitrobenzene (NB) can be removed in MFCs, but the removal can be significantly enhanced in MECs with a small amount of energy supply (Mu et al., 2009a). A membraneless, up-flow MEC-type reactor was developed to reduce NB (Wang et al., 2012). Up to 98% of NB was removed in the cathode zone with an external voltage supply of 0.5 V, resulting in a maximum removal rate of 3.5 mol/m^3/d. The main product from NB degradation was aniline and the production rate reached to 3.06 mol/m^3/d. The overall energy requirement for this process was less than 0.075 kWh/mol NB (Wang et al., 2012). As one of typical recalcitrant pollutants, azo dyes can also be removed from the cathode of MECs. Mu et al. (2009b) investigated the reduction of Acid Orange 7 (AO7) in MECs. AO7 reduction at cathode was achieved at rates up to 1.32 mol/m^3/d (net reactor compartment) without electricity input, and this rate was significantly improved to 6.59 mol/m^3/d with voltage input (at a controlled cathode potential of −400 mV vs SHE) (Mu et al., 2009b). The energy consumption for above process was up to 0.05 kWh/mol AO7, which was much lower than that required by conventional electrochemical reduction method (about 11.2 kWh/mol AO7) (Bechtold et al., 2001; Mu et al., 2009b).

Chlorophenols (CPs) is a particular group of chlorinated pollutants which are toxic, bio-refractory and difficult to be degraded in the natural environment. Wen et al. (2012) investigated the feasibility of 4-chlorophenol removal in two-chamber MFC and MEC. The 4-CP reduction process was feasible in the two-chamber MFC with a small amount of electricity production. However, the dechlorination efficiency of 4-CP at the cathode was only 50.3%. It was significantly enhanced to 92.5% when the reactor was operated in MEC mode with 0.7 V voltage input. The maximum dechlorination rate reached to 0.38 mol/m^3/d with an energy consumption of 0.549 kWh/mol 4-CP (Table 3) (Wen et al., 2012). The energy consumption of MECs for dechlorination was much lower than that of conventional electrochemical methods, where about 1.17 kWh/mol 4-CP of energy was required (Cheng et al., 1997). MECs have also been applied to dehalogenate trichloroethylene (TCE) and iodinated contrast medium diatrizoate ($diaI_3$) (Hennebel et al., 2011). With 0.8 V voltage supply, TCE was degraded into chloride and ethane at a rate of 0.58 mol/m^3 (reactor volume)/d with bio-Pd coated cathode (5 mg/g-electrode) in a MEC (Hennebel et al., 2011). Similarly, diatrizoate dechlorination was degraded into 3,5-diacetamidobenzoate which has less impact on environment (De Gusseme et al., 2011). Therefore, MECs offer an alternative and promising method to dehalogenate pharmaceutical, and thereby significantly decrease the environmental burden of pharmaceutical point-sources such hospital wastewaters (De Gusseme et al., 2011). Beside metal catalyzed cathode, the biofilm formed on the cathode as biocathode can significantly enhance the kinetics of the electron transfer reactions, and thereby enhance the removal of TCE. In a previous study, the dechlorination of TCE into cis-dichloroethene has been reported, where lower amounts of vinyl chloride and ethane were observed as end products at a maximum formation rate of 0.0112 mol/m^3/d (Aulenta et al., 2010).

3.2.2. *Inorganic pollutants*

Several inorganic pollutants such as sulphate, perchlorate and nitrate can also be removed at the cathode of MECs (Coma et al., 2013; Thrash et al., 2007; Zhan et al., 2012). Sulphate is one of the most abundant pollutants found in the water

Table 3 – A summary of pollutants treated by MECs and corresponding performances.

Pollutants	Reactor type	Treating chamber	Removal rate[a] (mol/m^3/d)	Input voltage (V)	Energy requirement (kWh/mol-pollutant)[b]	References
Nitrobenzene	Single chamber up-flow	Cathode	3.5	0.5	0.075	(Wang et al., 2012)
Acid Orange 7	Two-chamber MEC	Cathode	6.59	−0.4[c]	0.008–0.05	(Mu et al., 2009b)
4-chlorophenol	Two-chamber MEC	Cathode	0.38	0.7	0.549	(Wen et al., 2012)
TCE	Two-chamber MEC	Cathode	0.46	0.8	–[d]	(Hennebel et al., 2011)
	Two-chamber MEC	(Bio)Cathode	0.0112	−0.55[c]	–	(Aulenta et al., 2010)
diaI3	Two-chamber MEC	Cathode	0.005	0.8	–	(Hennebel et al., 2011)
Diatrizoate	Two-chamber MEC	Cathode	0.264	0.8	9.6	(De Gusseme et al., 2011)
Sulphate	Two-chamber MEC	(Bio)Cathode	0.011–0.33[e]	0.7–1.4	–	(Coma et al., 2013)
Perchlorate	Two-chamber MEC	Cathode	0.6	−0.253[e,c]	–	(Thrash et al., 2007)
Nitrate	Single chamber	Cathode	2.85	0.2–0.4	0.014[e]	(Zhan et al., 2012)
Nickel ion	Two-chamber MEC	Cathode	1.01	0.5–1.1	–	(Qin et al., 2012)

[a] Calculated on the basis of total reactor compartment.
[b] Energy consumption calculated on the basis of total reactor compartment.
[c] Controlled cathode potential vs SHE.
[d] Not available.
[e] Estimated according to the available data.

environment, which is commonly removed through biological processes. However, biological treatment requires large amounts of organic matter, which prevent its practical application. Recently, the reduction of sulphate as electron acceptor at a bacteria-catalyzed cathode in a MEC has been reported (Coma et al., 2013). Sulphate reduction was not observed without voltage supply, while the removal rate increased with the voltage applied and reached more than 50 g $SO_4^{2-}/m^3/d$ at 1.4 V. The minimum voltage requirement for such process is 0.7 V. The end product from sulphate reduction was sulphide which was entrapped in the ionic form due to the high pH in the cathode (Coma et al., 2013). With this approach, organic matter oxidation and sulphate reduction processes are physically separated, which prevent the competition for electrons from methanogenic bacteria. As there is no need of extra organic matters, this method is suitable for sulphate-contaminated groundwater treatment in order to avoid disturbing drinking water biostability (Coma et al., 2013). The main challenge of this method is the large pH gradient between the anode and cathode and the low conductivity of groundwater. In this context, boosted treatment performance could be expected by treating industrial wastewaters with high conductivity (Coma et al., 2013).

Perchlorate is a soluble anion which can affect mammalian thyroid hormone production and potentially lead to neonatal neuropsychological development deficiencies. It has been recently reported that perchlorate removal was facilitated at the cathode of MEC-like reactor in the presence of mediator (e.g., anthraquinone disulfonate) (Thrash et al., 2007). MECs offer a new solution for continuous treatment of similar critical contaminants in industrial wastewaters and drinking waters. Nitrogen removal in MFCs such as cathodic denitrification has been well studied previously (Clauwaert et al., 2007; Virdis et al., 2008). However, little information about nitrogen removal in MECs system is available. Recently, it has been reported that nitrogen removal can be enhanced in MECs (Zhan et al., 2012). The nitrogen removal efficiency in a single-compartment 3-dimensional MEC was improved from 70.3% to 92.6% when the voltage was increased from 0.2 to 0.4 V (Zhan et al., 2012). The DO level in MECs should be well controlled to make the technology field applicable, as nitrification process needs oxygen, while denitrification process at the cathode can be inhibited at high DO level. Since microorganisms on the anode can generate protons and electrons by complete oxidation of ammonia, the electric energy needed for nitrogen removal in MECs was greatly reduced compared to the water electrolysis process (Zhan et al., 2012).

Treatment of heavy metals contaminated wastewater has gained much attention recently because of the toxicity and difficult degradation properties of heavy metals. MECs have been demonstrated as an efficient and cost-effective method for treatment of wastewater containing heavy metals such as nickel ion (Ni^{2+}) (Qin et al., 2012). Compared to conventional electrolysis cells and MFCs, MECs achieved three times higher Ni^{2+} removal efficiency (Qin et al., 2012). The applied voltage and initial Ni^{2+} concentrations are two key factors for Ni^{2+} removal in the MECs (Qin et al., 2012). As a result of Ni^{2+} reduction, metal nickel (Ni^0) was observed as product on the cathode electrode according to the X-ray diffraction measurements (Qin et al., 2012). MECs can be an alternative process to conventional electrolysis method for treatment of Ni^{2+} containing wastewaters. To make this technology more applicable, several challenges still need to be addressed. The long-term stability of this system need to be explored, since the formation of metal nickel on the cathode surface might affect the cathode reaction activity and further affect the system performance. Recovery of the metal nickel from cathode surface is also an important issue.

It is obvious that MECs hold promising perspectives as an alternative technology for pollutants removal. However, there is still a long way before field application. In the most of the cases, as a treatment technology, MECs cannot completely convert the pollutant to clean products, especially for organic pollutants removal. Even the end product is less toxic than the original pollutant (e.g., nitrobenzene is reduced to Aniline (Mu et al., 2009a)), further treatment is still required. In this context, MECs could be a pretreatment method for other technologies such as aerobic process. Intensive studies in this area are still required, since there are several kinds of pollutants that could be potentially removed at the cathode of MECs. Study of the effectiveness of MECs on different types of pollutant will offer new perspective, and thus, will help for better understanding the mechanism and resulting in overall systematic optimization.

3.3. *Resources recovery*

Metals present in waste streams should be recovered in order to lower their threat to environment and reuse of finite resources. Several metal ions such as Cu^{2+} and Hg^{2+} have been tested as electron acceptors at the cathode of MFCs (Heijne et al., 2010; Wang et al., 2011). These metals can be recovered in MFCs with simultaneous electricity production, as they normally have high reduction potential (e.g., 0.34 V for Cu^{2+}) (Modin et al., 2012). However, for these metal ions with lower reduction potentials, recovery cannot be achieved in MFCs without extra energy supply. Since MECs hold several advantages such as low energy requirement compared to conventional electrochemical process, it could be an alternative method for energy-efficient metals recovery. MECs have been recently demonstrated for recovery of Cu, Pb, Cd, and Zn from a simulated municipal solid waste incineration ash leachate (Modin et al., 2012). The cell voltage required for the recovery of Cu, Pb, Cd, and Zn was 0, 0.34, 0.51, 1.7 V, respectively. The corresponding energy consumption for the recovery process was 0, 3.8, 7.7, 283.9 kWh/kg-metal, respectively (Modin et al., 2012). The relatively higher energy consumption for Zn recovery was probably due to the formation of hydrogen and cathodic overpotential, which could be reduced by capturing the hydrogen as byproduct. More recently, Jiang et al. (2014) reported cobalt (Co) recovery from Co(II)-containing wastewater with simultaneous hydrogen production in MECs. At applied voltages of 0.3–0.5 V, the Co and hydrogen yields reached to 0.81 mol Co/mol COD and 1.21–1.49 mol H_2/mol COD, respectively. However, the energy efficient for Co recovery was 22.5%, while the one for hydrogen production was over 170%. It was also found that the phosphate buffer was more suitable for Co recovery and hydrogen production compared to borate buffer. However, further study with real Co(II)-containing wastewater instead of artificial

buffer solution is required for better understanding the system. Furthermore, struvite might be formed on the cathode surface and thereby affecting the Co recovery, since three struvite ionic components (Mg^{2+}, NH_4^+, and PO_4^{3-}) were available in the cathode in aforementioned study. This hypothesis needs to be further verified.

MECs offer a new avenue to recover metals from contaminated streams, e.g., wastewater, with less energy consumption while simultaneously treating wastewater and extract valuable products. The applicability of this method to other metals such as Ag^+ and Hg^{2+} needs to be further investigated. In addition, an effective strategy should be adapted to prevent the falling off of the metals deposited on the cathode and returning to the treated solution again.

In addition to metals, MECs have the potential to recover other resources such as phosphorus and ammonium from wastewater. Phosphorous and ammonium are two of main pollutants in wastewater and also two essential nutrients for all forms of life, thus it will bring both environmental and economic benefit if they can be recovered and reused. Recently, a single chamber MEC has been tested as an energy efficient method to drive hydrogen production and struvite crystallization ($MgNH_4PO_4{-}6H_2O$) which is a renewable source of phosphorus (Cusick and Logan, 2012). 20%–40% of phosphorus removal was achieved and the crystals accumulated at the cathode were verified as struvite (Cusick and Logan, 2012). It was also observed that the hydrogen production was not affected by the struvite accumulation on the cathode. The crystal accumulation and hydrogen production rates were mainly dependent on applied voltage and cathode materials (Cusick and Logan, 2012). Thus, MECs can be a potential method for hydrogen gas and struvite production from phosphorus-rich wastewater. The energy produced in form of hydrogen could offset the energy consumption for phosphorus recovery. Future work could focus on the system optimization in order to improve the phosphorus removal. Furthermore, development of cathode electrode with large surface area such as carbon fiber brush or nanoelectrode-modified electrode might also lead to high struvite accumulation rate. Compared to phosphorus, ammonium recovery in MECs is through a different mechanism. A strategy to recover ammonium and simultaneously produce hydrogen from reject water in MECs has been recently developed (Wu and Modin, 2013). Instead of feeding the ammonium-rich reject water to the anode as what is normally done in MFCs, the reject water was directly fed to the cathode chamber of MECs where protons were reduced to hydrogen and the ammonium were recovered through volatilization at high cathode pH. Through this process, up to 94% of ammonium was recovered while up to 96% of electrical current was converted to hydrogen gas at the cathode (Wu and Modin, 2013). Compared to MFCs, MECs could be a more feasible method to recover ammonium in industrial level because of the high ammonia and energy recovery rate (Wu and Modin, 2013). The produced hydrogen can compensate part of electric energy cost used for driving the process and it also can contribute to the ammonia stripping and thereby lowering the energy cost on air stripping. However, this process may be more suitable for the wastewater containing high ammonium but with low organic content. Otherwise, the high pH in the cathode effluent might hinder the downstream processes (e.g., anaerobic digestion) for organic matters removal. An alternative process could be proposed that feeding the wastewater to the anode of MECs for organic removal first and then direct the effluent to the cathode for ammonium recovery. During the process, part of ammonium could migrate to the cathode depending on the membrane. Nevertheless, the potential toxicity of ammonium on anode bacteria should be taken into account (Nam et al., 2010). Although phosphorus and ammonium recovery in MECs were studied separately so far, these two processes could be combined in the light of the advantages of MECs. This concept could be interesting in future studies and would potentially offer a promising avenue for practical wastewater treatment and nutrients recovery.

3.4. *Bioelectrochemical research platform*

Because it can be easily constructed with commercially available materials and be powered simply by a power source, MECs have been applied as a simple platform for conducting high throughput bioelectrochemical research (Call and Logan, 2011). A small crimp top serum bottle (5 mL) with a graphite plate anode and different cathode (e.g., stainless steel mesh/wire) was used as a MEC. It was found that several MECs (>1000 reactors) can share a single power supply under parallel operation without any disturbance of performance. The applicability of this method for cultivation of electrochemically active microorganisms was investigated in view of the effect of buffer on pure or mixed cultures. High current density was always observed with mixed culture regardless of media applied. Relatively higher current was generated with 50 mM phosphate buffer compared to 30 mM bicarbonate buffer. Sustained current generation was only obtained with the mixed culture with a 200 mM phosphate buffer (Call and Logan, 2011). The miniaturized MECs have several advantages as a platform for conducting high throughput bioelectrochemical research. First, the small electrode spacing and separator-less design can reduce pH gradients and internal resistance. Second, reactor can be built based on cheap and commercially available materials. Third, this method allows for conducting high throughput research at a large scale. More than 6000 reactors could be operated in parallel with only one power supply (Call and Logan, 2011).

MECs have also been used to cultivate electrochemically active inoculum for MFCs. It was found that the air-cathode MFC cannot generate appreciable power from cellulose using a wastewater inoculum because the oxygen diffusion (Cheng et al., 2011). To avoid oxygen during biofilm development, microorganisms were firstly cultivated in a two-chamber, aqueous cathode MEC and then used as inoculum in two different types of air-cathode MFCs (Cheng et al., 2011). Successful power generation was observed in the air-cathode MFC with the inoculum cultivated in the MEC, which demonstrated that high power densities can be produced from cellulose-powered air-cathode MFCs by acclimating the inoculum in a proper way (Cheng et al., 2011). This observation is different from that in typical MECs studies, in which the inoculum of MECs is first acclimated in the anode of MFCs (Liu et al., 2005b; Logan et al., 2008). According to such observation, enhanced hydrogen production could be expected if the

biofilm on the anode of MECs is acclimated in MEC mode from the beginning. This hypothesis needs to be further verified.

Extracellular electron transfer (EET) is one of the most important and hottest topics of BES research. Until now, most of the works on EET are based on MFC platform. In light of the unique advantages of MECs, it will provide both new and experienced researchers with a powerful platform for conducting high throughput bioelectrochemical research such as study of EET mechanisms between bacteria and electrode or between different bacteria species.

3.5. Biosensor

MECs can also be used as a new type of biochemical oxygen demand (BOD) sensor. In previous studies, MFCs rather than MECs have been widely used as BOD sensors regarding the correlation between current generation and substrate concentration (Zhang and Angelidaki, 2011). However, the detection range of MFC-based sensor is always limited by the microbial kinetics, internal resistance and cathode oxygen reduction. To overcome these limitations, Modin et al. (2012) developed a new type of BOD sensor based on an MEC. The charge showed linear relationship ($R^2 = 0.97$) with BOD concentration ranging from 32 to 1280 mg/L in a reaction time of 20 h. The maximum BOD can be detected with the MEC is much higher that of MFC-based sensors (Zhang and Angelidaki, 2011). MECs show the potential to be a more robust and simple bioelectrochemical BOD sensor, which can overcome usual limitations of MFCs. However, one of main challenge for the practical application of this method is the energy consumption. Although the energy required by MECs is much lower than that of conventional electrochemical methods, the energy consumption is still high, especially for long-term operation. In above study, using an anaerobic cathode instead of air-cathode for hydrogen production might offset the energy consumption, which could be the focus of future study. Furthermore, owing to the advantages of MECs compared to MFCs as a biosensor, MECs could also be an alternative to MFCs as biosensor for monitoring microbial activity and toxicity, the feasibility of which need to be further explored.

3.6. Integration of MEC with other BESs for value-added applications

3.6.1. Microbial electrodialysis cell (MEDC)

Because of the advantages of low energy demand and high yield of hydrogen production, MECs have been integrated with other BESs such as microbial desalination cell (MDC) to boost the desalination performance and energy recovery (Luo et al., 2011; Mehanna et al., 2010). Mehanna et al. (2010) for the first time demonstrated the integration of MEC with MDC, and the new system was renamed as microbial electrodialysis cell (MEDC). Through such integration, the potentials between the electrodes, which is the driven force for ions transportation (e.g., Na^+ and Cl^-), can be better controlled. The hydrogen production can cover the electrical energy consumption on desalination, making the whole process self-sustainable (Mehanna et al., 2010). Therefore, simultaneous desalination and hydrogen production can be realized. Nearly at the same period, another research group developed similar technology called microbial electrolysis and desalination cells (MEDC) (Luo et al., 2011). Compared to the previous study, much higher H_2 production rate (1.5 m^3 $H_2/m^3/d$) from cathode chamber was obtained due to the relatively higher voltage added (0.8 V). Correspondingly, 98.8% removal of the10 g/L NaCl was observed (Luo et al., 2011). As a new technology, the MEDC is facing several challenges such as pH variation, high ohmic resistance due to the reduction of conductivity and membrane biofouling problem. Further investigation of such combined system with real seawater or wastewater instead of synthetic media/buffer solution in continuous operation is required to accelerate the technology development.

3.6.2. Microbial saline-wastewater electrolysis cell (MSC)

The MEDC was further modified by exchanging the position of anion exchange membrane (AEM) and cation exchange membrane (CEM) and renamed as MSC (Kim and Logan, 2013). In an MSC, electroactive biofilm on the anode degrade organic maters in saline wastewater, and hydrogen is produced at the cathode as what is done in an MEDC or MEC (Kim and Logan, 2013). Meanwhile, the electricity added will drive the transportation of cations and anions from the anode and cathode chambers respectively to the middle chamber, where more concentrated salt solution is produced. Unlike MEDC, MSC can simultaneously removal of organic matter and salt ions from saline wastewater. With 1.2 V applied potential, up to 84% of salinity (initial conductivity ~40 mS/cm) and 94% of chemical oxygen demand were removed at substrate concentration of 8 g/L (Kim and Logan, 2013). The main challenge of this technology is the adverse effect of high salinity on the exoelectrogens in the anode. It was found that exoelectrogenic activities were permanently damaged at high salinities (46 g-TS/L) (Kim and Logan, 2013). Therefore, several strategies such as selection of the inoculum with the tolerance to high salinity need to be developed in future study. The MSC offers a new avenue to achieve simultaneous H_2 production and removal of salinity and organic contaminants from a saline wastewater.

3.6.3. Microbial electrolysis desalination and chemical-production cell (MEDCC)

Although promising, the MDC, MEDC or MSC are individually facing several challenges. Firstly, the desalination process in these systems results in large pH differences in anode (pH decrease) and cathode (pH increase) chambers (Luo et al., 2011). The low pH (<5) in the anode chamber is harmful to the microbial activities, while the high pH in the cathode lower the hydrogen production rate. Secondly, high levels of Cl^- accumulated in the anode chamber may also inhibit the microbial activities (Chen et al., 2012; Mehanna et al., 2010). To solve these problems, Chen et al. (2012) propose a four-chamber reactor placing one bipolar membrane (BPM) between anode and AEM. The system is termed as MEDCC. When an electric field is added to the MEDCC, water is dissociated into OH^- and H^+ trough BMP, and then H^+ migrates into the acid-production chamber to produce acid while OH^- ions migrate into the anode chamber to retain the pH neutral. Meanwhile, cations in the desalination chamber transport to the cathode and combine with OH^- from oxygen reduction to produce alkali. With 1.0 V voltage supply, desalination efficiency of 86% was obtained in 18 h with 10 g/L NaCl (Chen

et al., 2012). With MEDCC, salty water is desalinated without the problem with large pH changes, and production of acid and alkali are achieved (Chen et al., 2012). Though MEDDC offers an insight into an efficient system for solving several limitations in MEDC or MDC, further improvement is still needed to make the technology practical applicable. For example, the H^+ leakage through AEM to desalination chamber need to be prevented by using more advanced membrane materials. Fresh water or other water sources with low salinity could be used in MEDDC to produce acid and alkali, as the solution with high NaCl levels may reduce the potential use of the products (Chen et al., 2012). Additionally, the feasibility of up-scale of this system still needs to be explored.

3.6.4. *Microbial reverse-electrodialysis electrolysis cell (MREC)*

Although the electricity required in above systems is much lower than that of conventional electrolysis process, the energy consumption is still high, which may limit their application especially in rural area where electricity is not reachable. Thus, a renewable source of the electricity is required to make MEDC or other similar technologies a sustainable and clean method for hydrogen production. In this context, Kim and Logan (2011) developed a unique method for hydrogen production based on combing a small reverse electrodialysis stack (five membrane pairs) into a MEC, and renamed it as MREC. In MREC, the energy for H_2 production is derived from microbial oxidation of organic matter in the anode and the salinity gradient between seawater and river water, and thus external power resources are not needed (Kim and Logan, 2011). The system achieved H_2 production rate of 1.6 m^3-H_2/m^3-anolyte/day with a seawater and river water flow rate of 0.8 mL/min. The energy consumption for water pumping is less than 1% with a small reverse electrodialysis stack (11 membranes) (Kim and Logan, 2011). MREC holds great potential as a sustainable method to treat wastewater and simultaneously produce pure hydrogen gas without consumption of electrical energy. As it is a new technology, it is still facing several challenges such as membrane fouling with seawater. The effectiveness of this system in large-scale operation also needs to be further elucidated. The availability of both fresh and salt waters is also important for the successful implementation of this technology. Thus, the most possible application of this technology is in coastal and not inland regions. To overcome area limitation and also to avoid membrane fouling with seawater, the researcher found a novel approach by using recycled sources of clean salt solutions such as ammonium bicarbonate (NH_4HCO_3) instead of seawater (Nam et al., 2012). It was shown that MREC can produce enough voltage for hydrogen production using ammonium bicarbonate salts, which can be easily regenerated using low-temperature waste heat (Nam et al., 2012). At an infinite salinity ratio, the maximum hydrogen production rate of 1.6 m^3-H_2/m^3/d (3.4 mol H_2/mol-acetate as yield) was obtained (Nam et al., 2012). The application area of MREC is greatly expanded by using ammonium bicarbonate salts. This system also offers a new method to capture energy from waste heat at low temperatures. Nevertheless, the energy recovery (10% in the reported study) still needs to be improved to make MREC a more efficient, mature and competitive technology. Further investigation of the system in upscale operation could also be the interest of future study.

4. Challenge and outlook

Despite the sections above outlined the wide range of applications of MECs (overviewed in Fig. 3) and their promising perspectives, it should be noted that, numerous hurdles need to be addressed before that field applications are economically

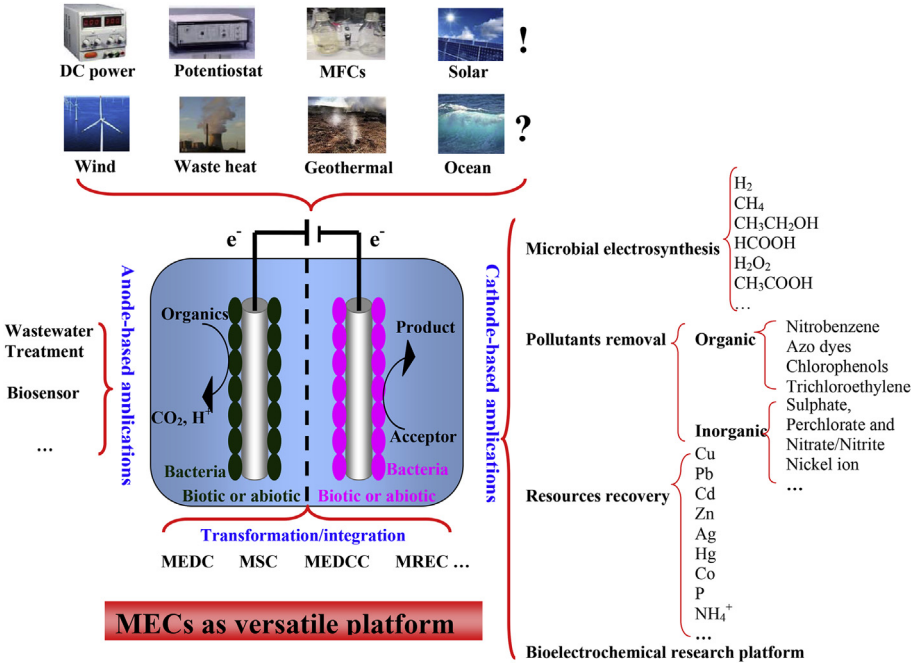

Fig. 3 – A high-level overview of the application niches of MECs. There are different choices of reactor configuration, membrane, electrode and catalyst at the anode and cathode according to different applications.

feasible. The challenges related to the different applications are discussed in previous sections. System upscaling of MECs is necessary in order to evaluate the industrial feasibility. The performance of MECs, especially for hydrogen production, seems satisfactory. However, complete new challenges respect to the cost and efficiency could be raised during scaling-up process. Scale-up of MECs from bench experiments to pilot-scale for hydrogen production has been recently reported. Though the electric energy recovery was above 70%, the Coulomb efficiency and hydrogen production rate are still much lower compared to the maximum value observed in lab-scale studies, indicating the necessary of further optimization (Gil-Carrera et al., 2012; Heidrich et al., 2013). Furthermore, other application possibilities of MECs such as chemicals synthesis, pollutants removal and metal recovery have not yet moved out from lab. Electrode materials and reactor design are two serious issues associated with scaling-up. Since MECs share the same anode reaction with MFCs, the cost-effective anode materials such as carbon fiber brush, carbon mesh or activated carbon, which are capable of efficient electron transfer from bacteria to electrode in MFCs could be an ideal option for MECs. Regardless of hydrogen production or other applications, the cathode electrode of MECs plays a critical role both in lowering overpotential and improvement of conversion rate. Carbon-based electrodes are a candidate regard of good stability and low cost. To further lower the overpotential and the overall internal resistance, catalysts are always needed. Platinum (Pt) is the best choice in respect of high catalysis activity and has been widely used in MECs studies. Generally, Pt is more suitable for foundation studies where a stable cathode activity is required. However, it is well accepted that Pt is not feasible for up-scaling application due to the high cost and negative environmental impacts (Kundu et al., 2013). Pt can also be poisoned by chemicals such as sulfide and thereby losing catalysis activities. Biocathode is deemed as promising alternatives to noble metals as cathode catalyst due to its low cost, good stability and environmental friendly property. However, the effectiveness of biocathode in pilot-scale operation is still unknown. In addition to cathode electrode and catalysis, catholyte is also important to MECs operation. It was suggested that NaCl solution and acidified water adjusted with sulfuric acid could be alternatives to phosphate buffer solution as catholyte by taking cost reduction and chemical reuse/disposal into account (Yossan et al., 2013). The rector design is also a key factor to up-scaling. Membrane-less single chamber MECs are widely used in lab studies. Though the construction cost is greatly reduced due to the removal of membrane, methane production is always observed due to the growth of methanogens, which make MECs inefficient for hydrogen production or other applications. This problem becomes more significant in pilot scale test. Cusick et al. (2011) developed the first pilot-scale (1000 L) continuous flow membrane-less single chamber MEC for simultaneous hydrogen production and winery wastewater treatment. Hydrogen production was observed at sub-mesophilic temperatures, but CO_2 was always detected and became dominant in the gas produced (51%). Even worse was that the system failed to produce hydrogen at mesophilic temperatures due to formation of methane via hydrogenotrophic methanogenesis (Cusick et al., 2011). The lesson learned from this work suggested that the purity of hydrogen and hydrogen losses due to methane formation are still the main challenges toward the practical application of membrane-less single chamber MECs. On the one hand, for the purpose of hydrogen production, better methods will be needed to suppress methanogenic growth and isolate hydrogen from other gas products (e.g., CO_2). On the other hand, considering that the percentage of CH_4 (86%) in the produced biogas was much higher than that of typical anaerobic digestion process (75%) (Cusick et al., 2011), membrane-less single chamber MECs are more suitable for CH_4 production. For the other applications such as ammonium recovery using membrane-less single chamber MECs, the ammonium toxicity on the anodic bioactivity needs to be taken into consideration.

Despite several challenges have to be overcome before commercial application, the fast growing application possibilities of MECs offers this versatile technology promising perspectives. Especially, the recent invention of microbial electrosynthesis provides an innovative option for efficient and sustainable chemicals production (Rabaey and Rozendal, 2010). MECs are developed base on MFCs, thus most of the advances achieved in MFCs can also be applied to MECs, thereby promoting the development of MECs. Summarizing, the following key-points need to be drawn for future work:

I. Application oriented reactor design is necessary to lower both construction costs and energy losses.
II. The application scopes of MECs could be further expanded e.g. for nutrients recovery.
III. Renewable and sustainable power sources are needed to make the whole process more cost-effective. In return, MECs could be an alternative method to store the extra renewable energy (e.g. electricity from windmill).
IV. The spectrum of pollutants treated with MECs could be even expanded, while the treatment capacity of MECs needs to be further improved.
V. The integration of MECs with existing separation, convention and treatment processes (e.g. anaerobic digestion) is helpful for overcoming drawback and bringing benefits to each other, and thereby boosting the waste conversion and energy production.

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