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REVIEW

A comprehensive review of microbial electrolysis cells (MEC) reactor designs and configurations for sustainable hydrogen gas production

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KEYWORDS

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Reactor design;
Hydrogen production rate (HPR);
Membrane;
Anode;
Cathode

Abstract Hydrogen gas has tremendous potential as an environmentally acceptable energy carrier for vehicles. A cutting edge technology called a microbial electrolysis cell (MEC) can achieve sustainable and clean hydrogen production from a wide range of renewable biomass and wastewaters. Enhancing the hydrogen production rate and lowering the energy input are the main challenges of MEC technology. MEC reactor design is one of the crucial factors which directly influence on hydrogen and current production rate in MECs. The rector design is also a key factor to up-scaling. Traditional MEC designs incorporated membranes, but it was recently shown that membrane-free designs can lead to both high hydrogen recoveries and production rates. Since then multiple studies have developed reactors that operate without membranes. This review provides a brief overview of recent advances in research on scalable MEC reactor design and configurations.

Contents

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Nomenclature

MEC	microbial electrolysis cell
HPR	hydrogen production rate
GHG	greenhouse gas
PEM	proton exchange membrane
H^+	proton
AEM	anion-exchange membranes
CMM	charge-mosaic membranes
BEAMR	bio-electrochemically assisted microbial reactor
MFC	microbial fuel cell
A_S	specific surface area
NH_3	ammonia gas
CEM	cation exchange membrane
COD	chemical oxygen demand
BESs	bioelectrochemical systems
SMP	soluble microbial products
CE	coulombic efficiency
CEA	cloth electrode assembly
TW	titanium wire
SS	stainless steel
dWW	domestic wastewater
GDE	gas diffusion electrode
Y_{H2}	hydrogen yield
DSSC	dye-sensitized solar cell
MRECs	microbial reverse-electrodialysis electrolysis cells
MDC	microbial desalination cell
MEDC	microbial electrodialysis cell
MSC	microbial saline-wastewater electrolysis cell
MEDCC	microbial electrolysis desalination and chemical production cell

1. Introductions-microbial electrolysis cells (MECs)

In 2003, Nobel Laureate Dr. Richard Smalley stated that "energy is the single most critical challenge facing humanity" [1]. The world is facing an epic dilemma. The majority of energy (>86%) is derived from fossil fuels (oil, coal, and natural gas), which are non-sustainable resources that at some point may be completely exhausted [2]. Furthermore, increasing concerns over the impacts of these resources on global climate, human health, and ecosystems around the world are prompting researchers to find renewable alternatives for meeting our growing energy demand [3]. Hydrogen has tremendous potential as a fuel and energy source. Burning hydrogen does not contribute to greenhouse gas (GHG) emissions, acid rain or ozone depletion due to the fact that its oxidation product is only H_2O vapors [4–6]. Furthermore, hydrogen is highly efficient: it has the highest energy content per unit weight among the gaseous fuels, energy content 120 MJ/kg for H_2, 44 MJ/kg

for gasoline, 50 MJ/kg for CH_4, 26.8 MJ/kg for ethanol [7–9]. Moreover, hydrogen can be derived from a wide variety of biomass-based substrates and domestic waste materials, so it can be cost-effective, clean, sustainable and renewable [10,11]. However, currently 96% of commercial H_2 produced today comes from fossil fuels via steam reforming, thermochemical conversion (pyrolysis) and gasification [12,13]. The development of advanced technologies for producing H_2 from biomass and other renewable energy resources that reduce environmental problems is now given high priority.

Microbial electrolysis cell (MEC) is a new and promising approach for hydrogen production from organic matter, including wastewater and other renewable resources [14,15]. MECs were discovered in 2005 by two independent research groups, one at Penn State University and the second at Wageningen University in the Netherlands [16,17]. In an MEC, electrochemically active bacteria oxidize organic matter and generate CO_2, electrons and protons. The bacteria transfer the electrons to the anode and the protons are released to the solution. The electrons then travel through a wire to a cathode and combine with the free protons in solution. However, this does not occur spontaneously. In order to produce hydrogen at the cathode from the combination of these protons and electrons, MEC reactors require an externally supplied voltage ($\geqslant$0.2 V) under a biologically assisted condition of pH = 7, T = 30 °C, P = 1 atm (1.01×10^5 Pa) [16]. This is done by the input of a voltage via a power supply. However, MECs require relatively low energy input (0.2–0.8 V) compared to typical water electrolysis (1.23–1.8 V). Schematic diagram of two-chamber MEC is shown in Fig. 1.

In case acetate is used as substrate in MEC, electrode reactions in both chambers are as follows:

Anode:

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \quad (1)$$

Cathode:

$$8H^+ + 8e^- \rightarrow 4H_2 \quad (2)$$

MECs are analyzed and compared in terms of current production, hydrogen production rates, hydrogen recoveries, and energy recoveries [16]. Current is typically normalized to either an electrode surface area (m^2) or the reactor volume (m^3), which allows for better comparison among different reactors than simply reporting the current (mA or A). Current directly relates to the hydrogen production rate as the electrons that travel to the cathode are eventually converted into hydrogen gas. The use of high surface area anodes, close electrode spacing, different membrane materials, and improved reactor designs has rapidly increased both current densities and hydrogen recoveries in MECs [18,19].

Over the past decade, MECs as a new source of biofuels have been extensively reviewed. These include an update information on inoculum sources, electrode materials, architectures, performance, and energy efficiencies of these MEC systems [14,20], cathode material and catalysts suitable for generating H_2 in MECs [21], the recent advances on MECs mechanisms and operations [22], substrates used in MECs [23], the new applications of MECs and their resulting performance, current challenges and prospects of future [24,25], the biocathodes in MEC: present status and future prospects [26,27], separators used in microbial electrochemical technologies: current status and future prospects [28]. The mechanism of external electron transfer from two main bacteria in BES studies, *Geobacter sulfurreducens* and *Shewanella oneidensis* was described in great detail [29].

However, a comprehensive review on the reactor configurations of MECs is still lacking. In this article, we have reviewed all the MEC reactor designs which have been tested for generating H_2 in MECs so far.

2. Innovative MEC reactor configurations

2.1. Tow-chamber MECs

In all of the MEC studies listed below, a key component has always been the inclusion of a membrane, which presumably is used to improve the purity of the produced hydrogen and to prevent microbial consumption of the hydrogen. Substantial potential losses have been attributed to the inclusion of a membrane, along with hydrogen diffusion across the membrane and into the anode. The use of a membrane not only reduces the crossover of fuels and bacteria from the anode to the

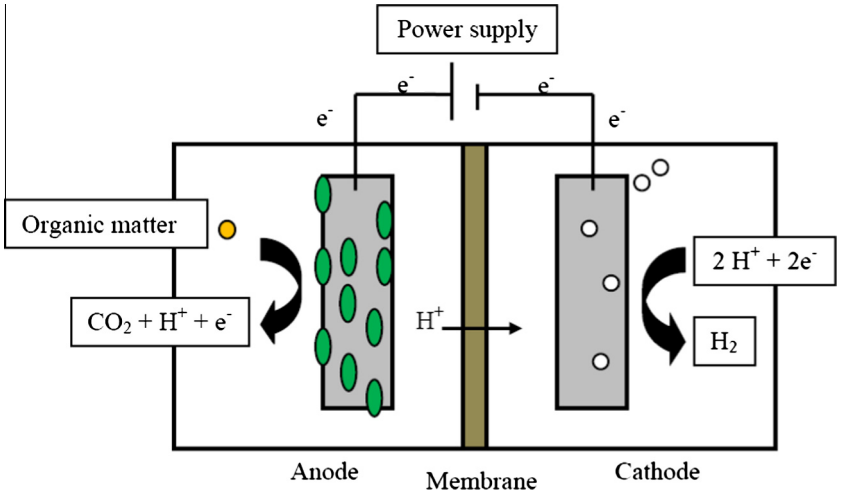

Figure 1 Schematic of typical two chamber MEC construction and operation.

cathode chamber and helps maintain the purity of the hydrogen gas evolved at the cathode, but also functions as a separator to avoid any short circuit. Various membranes have been used in microbial electrolysis cells, and the most common membrane is a proton exchange membrane (PEM) which is designed using $-SO^{3-}$ functional groups to only allow free protons (H^+) to pass [30,31]. Other membranes have also been tested in MECs, including anion-exchange membranes (AEM), such as AMI-7001 [32,19], bipolar membranes and charge-mosaic membranes (CMM) [33].

2.1.1. First bio-electrochemically assisted microbial reactor (BEAMR)

To prove the efficiency of this bio-electrochemically assisted process, Liu et al. [16]. Constructed two different hydrogen-generating reactors by adapting MFC reactor designs, both reactors were two-chamber MECs with the anode and cathode each in a chamber separated by a proton exchange membrane (Fig. 2A). The anode was plain carbon cloth and the cathode was made of carbon paper containing 0.5 mg Pt/cm^2. The first system was a two-bottle reactor (0.31 L capacity each) with the PEM held by a clamp in the tube separating the chambers, with electrodes spaced 15 cm apart. Instead of sparging the cathode chamber with air, the chamber was sealed and analyzed periodically for hydrogen gas production. Each electrode was 12 cm^2 and the PEM was 3.5 cm^2, and the bottles were filled to 0.2 L (Fig. 2).

Hydrogen gas was sampled and collected via sampling ports at the top of the MEC reactors. Hydrogen production via bacterial fermentation is currently limited to a maximum of 4 moles of hydrogen per mole of glucose, and under these conditions results in a fermentation end product (acetate; 2 mol/mol glucose) that bacteria are unable to further convert to hydrogen. It is shown here that this biochemical barrier can be circumvented by generating hydrogen gas from acetate using a completely anaerobic microbial fuel cell (MFC). By augmenting the electrochemical potential achieved by bacteria in this MFC with an additional voltage 0.25 V or more, it was possible to produce hydrogen at the cathode directly from the oxidized organic substrates. More than 90% of H^+ and electrons produced by the bacteria from the oxidation of acetate were recovered as hydrogen gas, with an overall coulombic efficiency (CE) of 60–78%. This is equivalent to an overall yield of 2.9 mol-H_2/mol-acetate. Production of hydrogen by this anaerobic MFC process is not limited to carbohydrates, as in a fermentation process, as any biodegradable dissolved organic substrates can theoretically be used in this process to generate hydrogen gas.

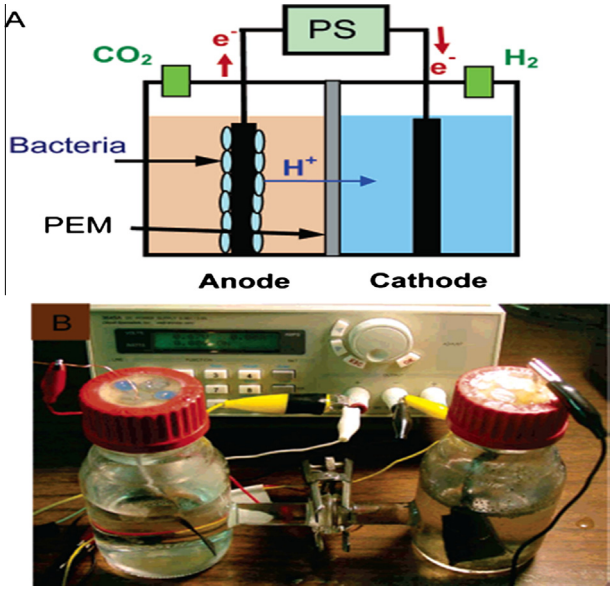

Figure 2 (A) Generalized schematic of first bio-electrochemically assisted microbial reactor (BEAMR), showing two chambers separated by a proton exchange membrane (PEM) with the voltage set using a power supply (PS). (B) Laboratory-scale prototype of the reactor based on using two bottles with the PEM held in a tube between the two chambers.

2.1.2. A new and high-performance MEC

A new type of MEC reactor was designed by Cheng and Logan [32,34]. The MEC reactor was constructed by clamping an AEM (AMI-7001) between the anode (30 mm in diameter, 20 mm long; 14 mL) and cathode (40 mm long; 28 mL) chambers. The anode chamber was filled with graphite granules which were 2–6 mm in diameter at a specific surface area of A_s = 1320 m^2/m^3, calculated as $A_s = 6\ Q/d$, where d = 4 mm is the average particle diameter and Q = 53% is the bed porosity. The granules were pre-treated with a high temperature ammonia gas (NH_3) process which increases current densities and reduces reactor acclimation times [35]. The cathode was made of carbon cloth and a Pt catalyst 0.5 mg/cm^2 Pt; prepared as previously described [36], and it was placed in the cathode chamber close to the membrane and connected to the external circuit by a titanium wire (0.68 mm in diameter; Alfa Aesar) (Fig. 3).

H_2 was collected by gluing the open bottom of a glass tube (80 mm long by 16.8 mm in diameter; empty bed volume of 0.018 L) containing a crimp top with a thick rubber stopper to a hole cut into the top of the cathode chamber. By improving the materials and reactor architecture, hydrogen gas was produced at yields of 2.01–3.95 mol at applied voltages of 0.2–0.8 V using acetic acid, a typical dead-end product of

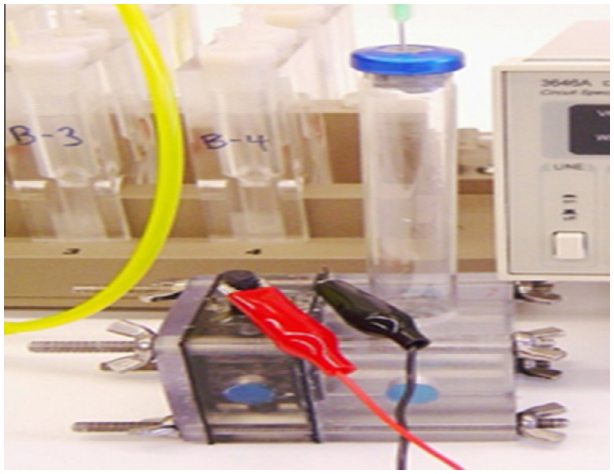

Figure 3 Generalized schematic of a two-chamber MEC (developed by Chen and Logan 2007).

glucose or cellulose fermentation. At an applied voltage of 0.6 V, the overall energy efficiency of the process was 288% based solely on electricity applied, a hydrogen production rate (HPR) of 1.1 m^3 H_2/m^3 d.

2.1.3. Concentric tubular MEC

A dual-chamber MEC reactor was designed by Kyazze et al. [37]. It consisted of two concentric tubular chambers. The inner tube was radially perforated on one side of the tube and inserted into the larger outer tube. The inner tube contained an anode electrode assembly rolled several times around a plastic inner rod. A cation exchange membrane (CEM) was wrapped around the outer surface of the inner tube to cover the perforations, thus forming a partition between the internal volumes of the two tubes. The cathode assembly was wrapped around the CEM (Fig. 4).

The highest HPR was obtained at an applied voltage of 0.85 V. The CE and cathodic hydrogen recovery were 60% and 45% respectively. Hydrogen yield (Y_{H2}) was up to 1.1 mol for each mole of acetate converted, corresponding to 30.5% chemical oxygen demand (COD) reduction.

2.1.4. Enrichment of MEC bio-cathodes from sediment MFC bio-anodes

Two sediment type microbial fuel cells (MFCs) consisting of glass test tubes (1.8 cm wide by 15.0 cm deep) were filled to a depth of 5 cm with sediment from each site. Heat-treated graphite fiber brush anodes (25 mm in diameter by 25 mm in length; 0.22 m^2 surface area) were inserted 1 cm below the sediment surface. The anode was connected by an insulated titanium wire containing a resistor to an upper air cathode positioned near the air–water interface at the upper opening of the test tube. The air cathode was 30% wet proofing (type B) coated with a Pt catalyst layer (0.5 mg of Pt/cm^2) carbon cloth. Each MFC contained an Ag/AgCl reference electrode (Fig. 5) [38].

There was abundant microbial growth in the biocathode chamber, as evidenced by an increase in turbidity and the presence of microorganisms on the cathode surface. The transfer of suspension to steriled cathodes was made of graphite plates, carbon rods, and carbon brushes. New bioelectrochemical systems (BESs) results showed the growth by these microbial communities on a variety of cathode substrates.

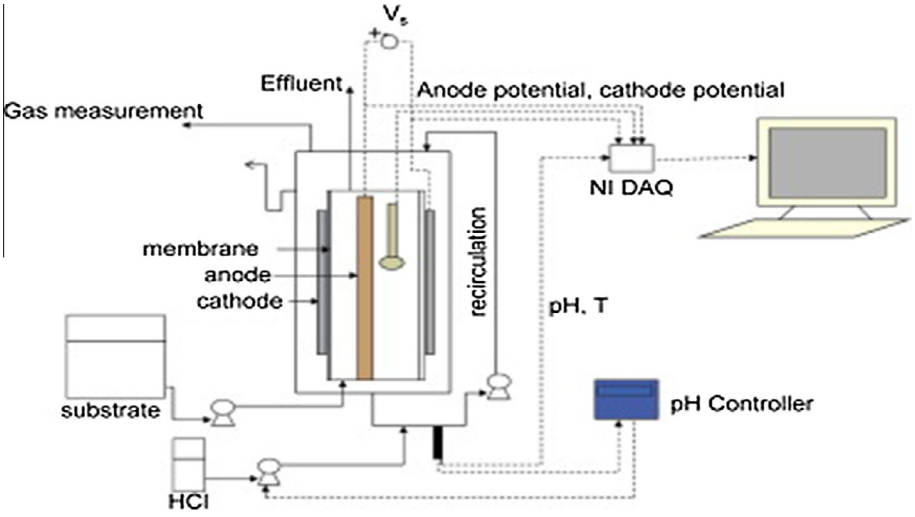

Figure 4 A schematic of the MEC setup in this study.

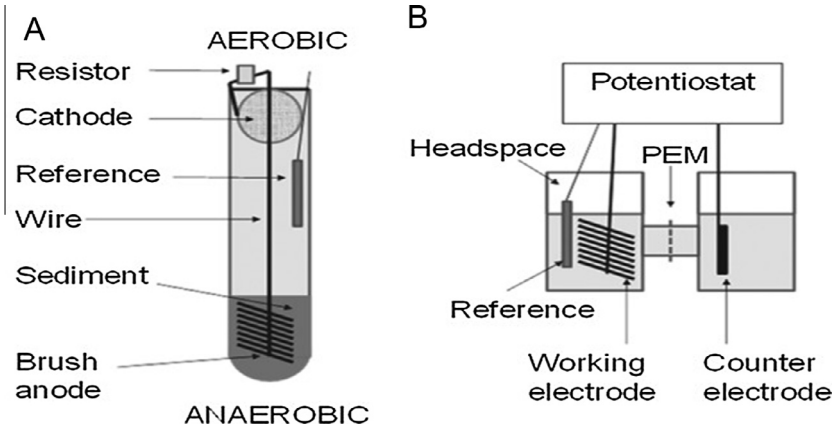

Figure 5 Two-step method used to first enrich (A) a diverse, electrically active sediment biofilm on MFCs brush anode that was then transplanted to form (B) the working electrode of a dual-chamber, potentiostat-controlled BES, or microbial half-cell.

2.1.5. Implication of endogenous decay current and quantification of soluble microbial products (SMP) in MEC

A two-chamber MEC was developed by An and Lee [39] which provided a large anode surface area against membrane surface area, while keeping a short distance between the anode and the cathode.

Current density ranged from 8.3 to 11 A/m^2 of membrane surface area, loading rate 0.3–6.3 kg COD/m^3 d. Hydrogen recovery was as high as 93 ± 25%, and HPR ranged from 66.4 ± 18.0 to 137.2 ± 14.4 L H_2/m^3 d at an applied voltage of 0–1.2 V. As a result, H_2 production costs were computed at 0.17–0.25 $/$m^3$ H_2 (1.7–2.6 $/kg H_2 at 25 °C and 1 atm) in the MEC using stainless steel mesh cathode.

2.2. Single-chamber MECs

Since hydrogen is relatively insoluble in water (0–1.5 mg/L at T = 25 °C and P_{H2} = 1 bar) and if production rates are high enough, it is likely that microbial conversion of hydrogen to methane will be slow [40]. Also, since MECs are completely anaerobic as opposed to MFCs, removing the membrane will not introduce oxygen to the anode and thus should not negatively impact efficiency of MEC. To reduce the potential losses associated with membrane and increase the energy recovery of this process, a new MEC design lacking a membrane was tested using several features such as ammonia-treated anodes, high surface area graphite brush anodes, and short electrode distance. Single chamber membrane-less MECs can be operated without membranes, thus simplifying architecture and reducing capital costs. However, one of the major issues with the absence of the membrane in MECs is the microbial hydrogen losses to methanogens. Methanogens compete with electrochemically active bacteria for both substrate (CH_3COONa) and product (H_2) [25].

2.2.1. A single chamber MEC with a brush anode and a flat carbon cathode

Call and Logan [18] developed a new MEC which lacking a membrane. The MEC was constructed from polycarbonate cylindrical chamber 4 cm long and 3 cm in diameter. The anode was an ammonia-treated graphite brush (25 mm diameter × 25 mm length; 0.22 m^2 surface area), with a specific surface area of 18,200 m^2/m^3 and porosity of 95%, placed into the center of the chamber. The cathode was wet-proofed (30%) carbon cloth, with a surface area of 7 cm^2 and a platinum (Pt) catalyst (0.5 mg/cm^2), placed on the opposite side of the chamber.

Gas produced at the cathode in the MEC bubbled into the reactor solution and the gas was collected using an anaerobic tube (headspace volume of 0.015 L) glued to the top of the reactor above an opening 1.6 cm in diameter. The top of the tube was sealed with a butyl rubber stopper and an aluminum crimp top. All the MEC reactors were covered with aluminum foil to exclude light (Fig. 6).

The cathodic hydrogen recoveries of 78 ± 1% to 96 ± 1% were achieved in an MEC, despite the absence of a membrane between the electrodes at applied voltages of 0.3–0.8 V and 7.5 mS/cm of solution conductivity. Through the use of a membrane-less system, a graphite fiber brush anode, and close electrode spacing, HPR reached a maximum of 3.12 ± 0.02 m^3 H_2/m^3 reactor per day at an applied voltage of 0.8 V. This production rate is more than double that obtained in previous MEC studies.

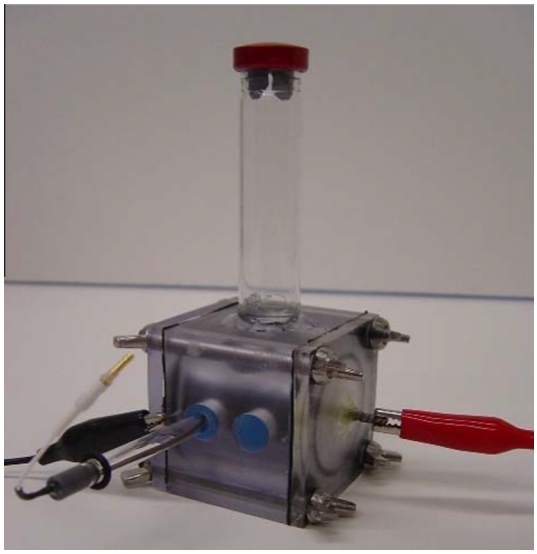

Figure 6 Single-chamber MEC with glass collection tube (top), Ag/AgCl reference electrode.

2.2.2. Bottle-type single-chamber MEC

Two kinds of single-chamber membrane-free MECs were constructed to investigate the hydrogen production efficiency of the systems (Fig. 7) [41].

The first system (a) was made from wide mouth glass bottles (0.5 L) and used to investigate hydrogen production by a mixed culture (Fig. 7a). The anode (3.5 × 4 cm^2) and cathode (4 × 5 cm^2) were held together by plastic screws with electrodes spaced 2 cm apart. The second system (b) was made from clear borosilicate glass serum vials (0.1 L) and used to investigate hydrogen production by *S. oneidensis* (Fig. 7b). Serum vials were chosen for the pure culture test mainly because they are easily sealed and autoclaved, and maintaining anaerobic condition after autoclave. The anode and cathode (both in 3 × 3 cm) in this system were separated by a layer of J-Cloth to avoid short circuit. For both systems, the anode was made of type A carbon cloth and the cathode was type B carbon cloth containing 0.5 mg/cm^2 Pt catalyst. Titanium wire (TW) was used to connect the electrodes with the circuit. At an applied voltage of 0.6 V, this MEC system with a mixed culture achieved a HPR of 0.53 $m^3/day/m^3$ (0.11 $m^3/day/m^2$) with a current density of 9.3 A/m^2 at pH = 7 and 0.69 $m^3/day/m^3$ (0.15 $m^3/day/m^2$) with a current density of 14 A/m^2 at pH = 5.8.

2.2.3. A cathode on top single-chamber MEC

The reactor consists of a main chamber and a top cover, both made of glass with an empty volume of 0.4 L (Fig. 8) [42].

The anode was graphite granules with a diameter of 3–5 mm, placed on the bottom of the chamber (0.3 L). The cathode was made of mipor titanium tube (inner diameter 20 mm, outer diameter 30 mm, height 50 mm, mipor diameter 10 μm) coated with platinum, placed in the top of the chamber. The closest distance between the anode and the cathode was 30 mm. A power source (IT6322, ITECH, Nanjing, China) was connected to the circuit to provide voltage, and a data

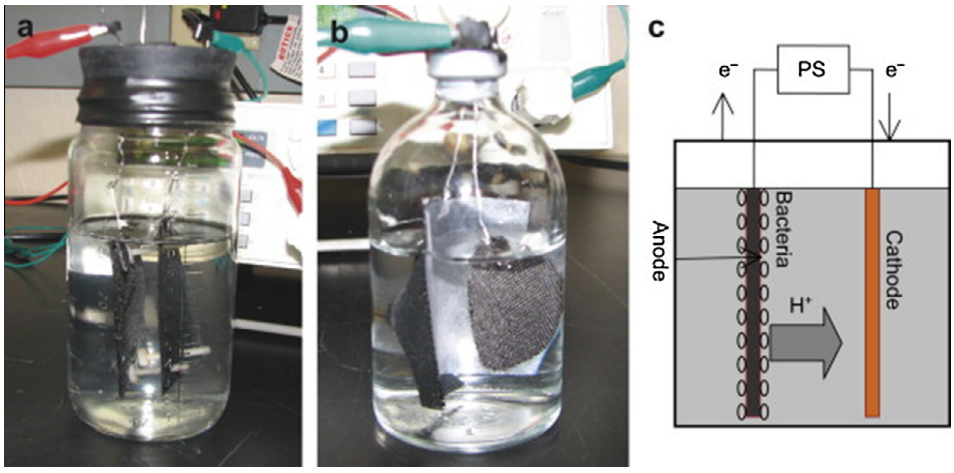

Figure 7 Photographs (a, b) and schematic (c) of single-chamber membrane-free MECs.

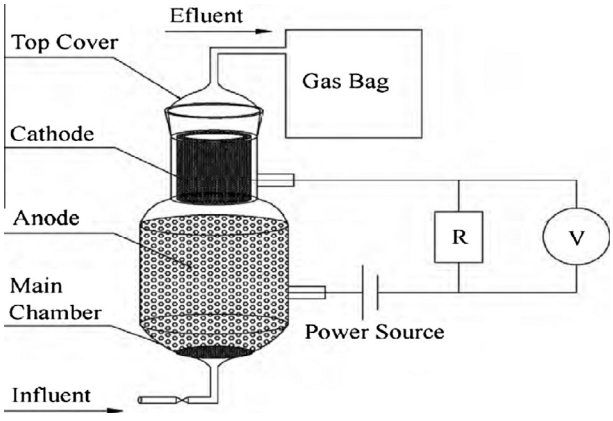

Figure 8 Schematic of the cathode-on-top single-chamber MEC.

acquisition board (AD8201H, Ruibohua Co., Beijing, China) was used to monitor the voltage across an external resistor to calculate the current. The electrolyte and substrate were pumped into the chamber through the bottom inlet, and the gas produced at the cathode was collected by using a gas bag. In 24 h batch tests, when the applied voltages increased from 0.2 V to 1.0 V, the HPR increased from 0.03 L/L/d to

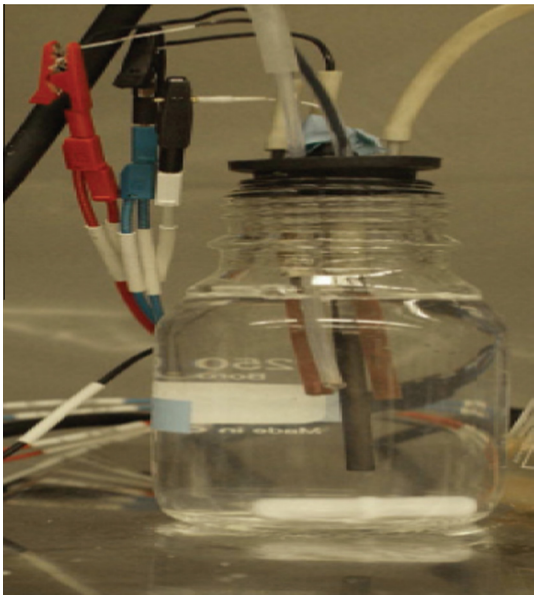

Figure 10 Bottle-type MECs with graphite rod electrodes.

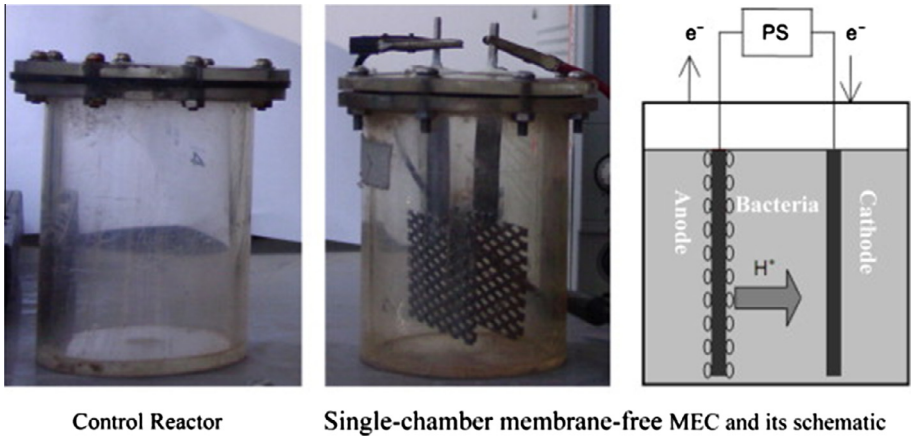

Figure 9 Single-chamber membrane-free MECs reactor used in the study.

1.58 L/L/d, and the overall hydrogen recoveries increased from 26.03% to 87.73%. The maximum overall energy recovery was 86.78% at the applied voltage of 0.6 V.

2.2.4. The anaerobic digestion of sewage sludge in single-chamber MEC

The single-chamber MECs were fabricated in the laboratory using Plexiglass, with a total volume of 0.3 L [43]. The anode ($4.0 \times 5.0 \times 0.2$ cm) and cathode ($4.0 \times 5.0 \times 0.2$ cm) were made of Ti/Ru alloy mesh plates and placed in the reactors. The distance between the anode and cathode was 20 mm. The cells were equipped with a gas and sludge sampling port. A cell without electrodes was used as a control (Fig. 9).

Hydrogen and methane were produced from the anaerobic digestion of sewage sludge in all reactors. Compared with controls, hydrogen production was enhanced 1.7–5.2-fold, and methane production 11.4–13.6-fold with Ti/Ru electrodes at applied voltages of 1.4 V and 1.8 V, respectively. Most of hydrogen was produced in the first 5 days of digestion and most of methane was generated after 5 days.

2.2.5. An up-flow single-chamber MEC

With the goal of maximizing the H_2 harvesting efficiency, Lee HS developed an up-flow single-chamber MEC by placing the cathode on the top of the MEC and carried out a program to track the fate of H_2 and electron equivalents in batch experiments (Fig. 10) [44].

When the initial acetate concentration was 10 mM in batch-evaluation experiments lasting 32 h, the CE was 60 ± 1%, the H_2 yield was 59 ± 2%, and methane production was negligible. However, longer batch reaction time (approximately 7 days) associated with higher initial acetate concentrations (30 or 80 mM) led to significant H_2 loss due to CH_4 accumulation: up to 14 ± 1% and 16 ± 2% of the biogas at 30 and 80 mM of acetate, respectively.

2.2.6. Single-chamber glass tubular MEC using non-precious metal cathode

The newly developed cathodes were tested in tubular membrane-free MECs for hydrogen production. The MECs were constructed with clear borosilicate glass serum tubes

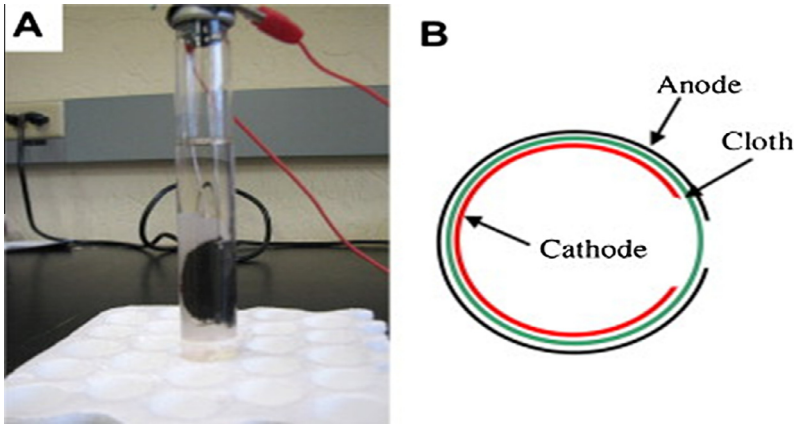

Figure 11 Photograph (A) and schematic of the cross section (B) of a single-chamber tubular MEC.

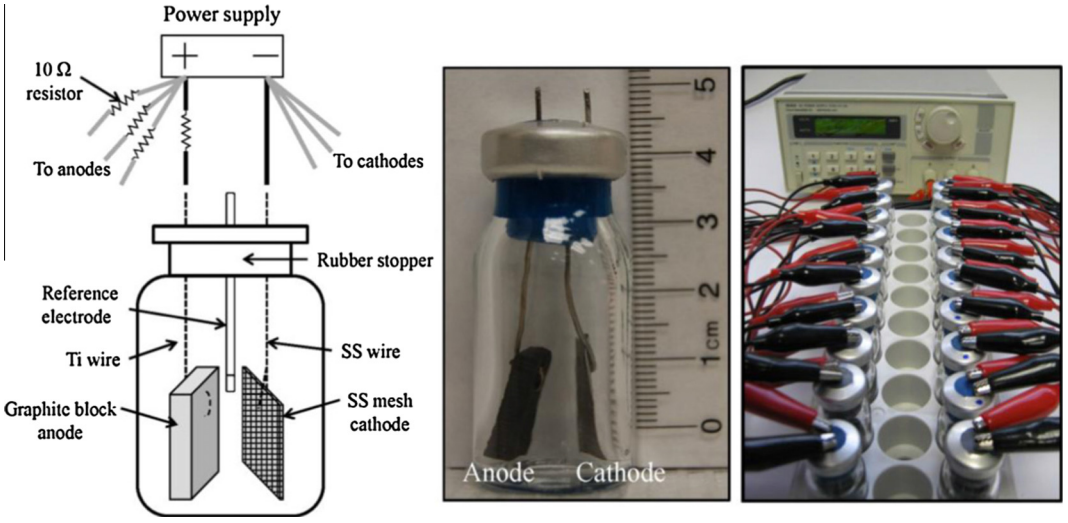

Figure 12 Schematic (left) and photographs of MEC design (middle) and parallel operation setup (right) using single power supply located behind reactors.

(0.28 L) (Fig. 11A). Carbon cloth 3 cm in diameter type A with biofilms developed in MFCs was used as anode and separated from the cathode ($2 \times 2\ cm^2$) by a layer of cloth ($4 \times 4\ cm^2$), forming a cloth electrode assembly (CEA) structure [45] (Fig. 11B). The development of biofilms on anodes was conducted in single-chamber MFCs as described previously [41,46]. When stable voltage output of the MFCs was obtained, and the MFC anodes were removed and placed in the tubular MECs. TW was used to connect the circuit (Fig. 11).

In this study, none-precious metal cathodes were developed by electrodepositing NiMo and NiW on a carbon fiber-weaved cloth material and evaluated in electrochemical cells and tubular MECs with CEAs. While similar performances were observed in electrochemical cells, NiMo cathode exhibited better performances than NiW cathode in MECs. At an applied voltage of 0.6 V, the MECs with NiMo cathode accomplished a HPR of $2.0\ m^3/day/m^3$ at current density of $270\ A/m^3$ ($12\ A/m^2$), which was 33% higher than that of the NiW MECs and slightly lower than that of the MECs with Pt catalyst ($2.3\ m^3/day/m^3$). At an applied voltage of 0.4 V, the energy efficiencies based on the electrical energy input reached 240% for the NiMo MECs.

2.2.7. The smallest scale MEC

A simple MEC system for conducting high throughput bioelectrochemical research was built with commercially available materials and operated using a single power source [47]. MECs were constructed using 0.005 L clear glass serum bottles. Anodes were isomolded graphite plates with a thickness of 0.32 cm, cut to dimensions of 1.5 cm (L) × 1 cm (W) (Fig. 12).

All anodes were polished using sandpaper, cleaned by soaking in 1N HCl overnight and rinsed three times in Milli-Q water. TW (0.08 cm diameter), cleaned with sandpaper, was cut to 5 cm lengths and bent at one end into a J-shape. After inserting the non-bent portion of the wire through a hole drilled near the top center of the graphite plate (0.08 cm diameter drill bit), the bent end was inserted into a second hole and crimped to provide a tight connection of the wire to the plate. Other materials, including carbon cloth and carbon paper, did not yield secure connections when crimped with wire and therefore were not used due to unacceptably large contact resistances. The highest volumetric current density of $240\ A/m^3$ was obtained using a stainless steel (SS) mesh cathode and a wastewater inoculum (acetate electron donor) at applied voltage of 0.7 V.

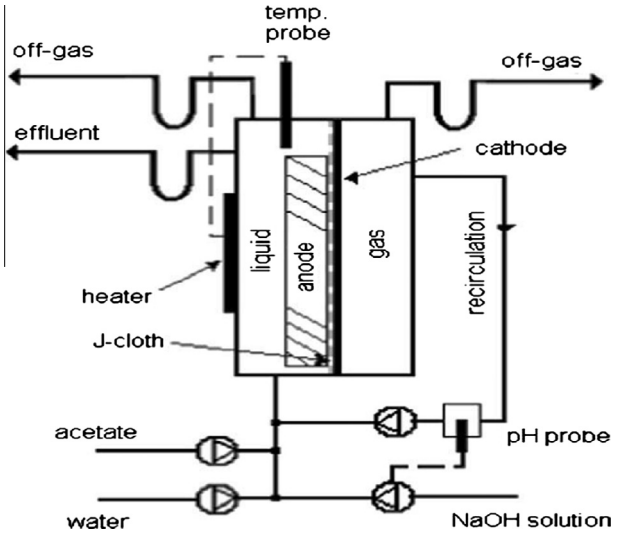

Figure 13 Diagram of a continuous flow MEC setup.

2.3. Continuous flow MECs

2.3.1. High rate membrane-less MEC for continuous hydrogen production

In this study, all experimentations were carried out in continuously fed MECs. Two cells were constructed, each with a series of polycarbonate plates arranged to form an anodic chamber and a gas collection chamber. Each chamber had a volume of 0.05 L. The cells were equipped with lines for influent, effluent, liquid recirculation and gas exits (Fig. 13) [48]. Temperature and pH were controlled at 25 °C and pH = 7, respectively.

This study demonstrates hydrogen production in a membrane-less continuous flow MEC with a gas-phase cathode. The MEC used a carbon felt anode and a gas diffusion

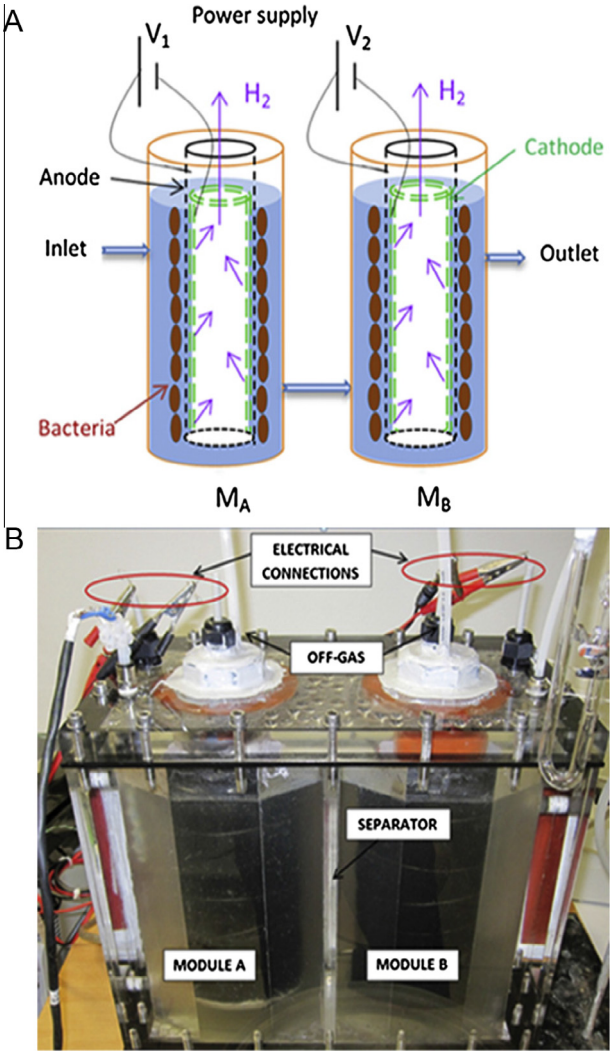

Figure 14 View of the two-module tubular MEC used in the experiments.

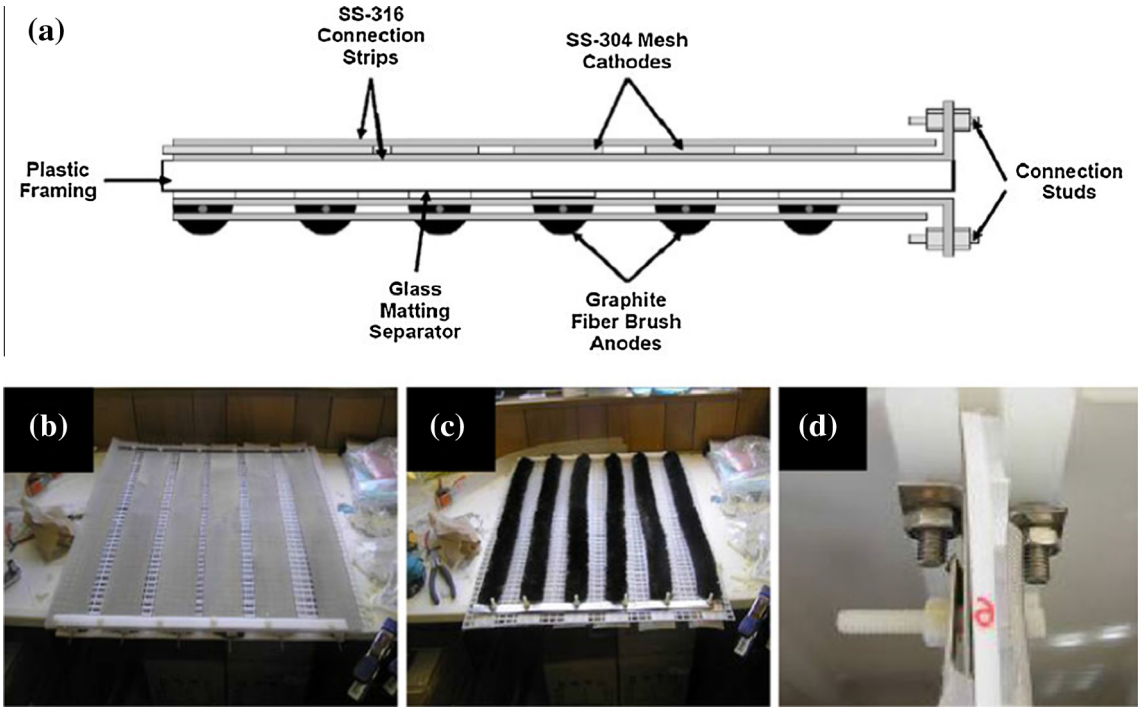

Figure 15 (a) Schematic of constructed electrode modules and pictures of (b) cathode side and (c) anode side of a module as well as (d) bolting within the reactor.

Figure 16 Laboratory-scale prototype of the MEC–MFC-coupled system.

cathode, and no proton exchange membrane was used in the setup. Instead, the electrodes were separated by a J-cloth. The absence of a PEM as well as a short distance maintained between the electrodes (0.3 mm) resulted in a low internal resistance. Due to an improved design, the volumetric HPR reached 6.3 $L_{STP}\ L_A^{-1}\ d^{-1}$.

2.3.2. A semi-pilot tubular MEC and domestic wastewater (dWW) treatment

Gil-Carrera et al. [49] examined the effect of the organic loading rate and the configuration of a semi-pilot modular MEC on the energy consumption during dWW. All tests were conducted in duplicate and performed in a continuous-flow

single-chamber MEC, which consisted of two tubular modules (MA and MB, 2 L each), connected in series. From the inside to the outside, each module consisted of the following. (i) A polypropylene tube 23 cm long, 12 cm diameter, with equally spaced 2 cm diameter holes at 1 cm intervals served a gas collection chamber. (ii) A 23 cm × 36.5 cm gas diffusion electrode (GDE) was wrapped around the polypropylene tube. The cathode was electrodeposited with nickel prior to use. A 2 m long and 0.125 mm thick titanium wire coiled around the electrode was used as a current collector. (iii) A 23 cm × 37 cm piece of porous cellulosic non-woven fabric with a thickness of 0.7 mm served as electrical insulation between the anode and the cathode. (iv) Two layers of 24 cm × 40 cm carbon felt served as the anode. The optimum thickness of the anode (1 cm) was selected based on the results from a previous study. Again, a 2.2 m long and 0.125 mm thick titanium wire coiled around the electrode served as the anodic current collector. Every unit was immersed in a 24.5 cm × 15 cm × 15 cm enclosure. The empty space between the anode and the inner walls of the receptacle served as the anodic chamber, retaining 2 L of liquid with a headspace of 0.2 L (Fig. 14).

The MEC reactor was able to reduce up to 85% of the COD of a dWW, with net energy consumption lower than that typically associated with aerobic treatments of dWW.

2.3.3. First pilot-scale continuous flow MEC for simultaneous hydrogen production and winery wastewater treatment

A pilot-scale (1000 L) continuous flow MEC was constructed and tested for current generation and COD removal with winery wastewater. The reactor contained 144 electrode pairs in 24 modules [50]. Twenty-four electrode modules were operated in parallel within the MEC, with each electrode module containing six anodes and six cathodes for a total of 144 electrode pairs. The electrodes were positioned on opposite sides of a 0.7 × 0.6 m perforated plastic frame. Strips of glass fiber matting (1 mm × 5 cm × 0.7 m) were placed between the anode and plastic frame to prevent short circuiting between electrode pairs. Anodes were made of graphite fiber brushes (D = 5.1 cm, L = 66 cm) and cathodes were made of SS 304, (W = 7.6 cm, L = 66 cm). Prior to use, all 144 anodes were heat treated. Optimal heat treatment in the laboratory for the brush anodes was reported as 450 °C for 30 min [51]. The anodes and cathodes of each module were electrically connected in series (Fig. 15).

At applied voltage of 0.9 V, current generation reached a maximum of 7.4 A/m^3. Gas production reached a maximum of 0.19 ± 0.04 L/L/day, although most of the product gas was converted to methane (86 ± 6%). In order to increase hydrogen recovery in future tests, better methods will be needed to isolate hydrogen gas produced at the cathode.

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

3.1. An MEC–MFC coupled system for biohydrogen production

Sun et al. [52] demonstrated the possibility of using an MEC–MFC-coupled system for hydrogen production from acetate, in which hydrogen was produced in an MEC and the extra power was supplied by an MFC. In this coupled system, hydrogen was produced from acetate without external electric power supply (Fig. 16).

At 10 mM of phosphate buffer, the HPR reached 2.2 ± 0.2 mL L^{-1} d^{-1}, the cathodic hydrogen recovery and

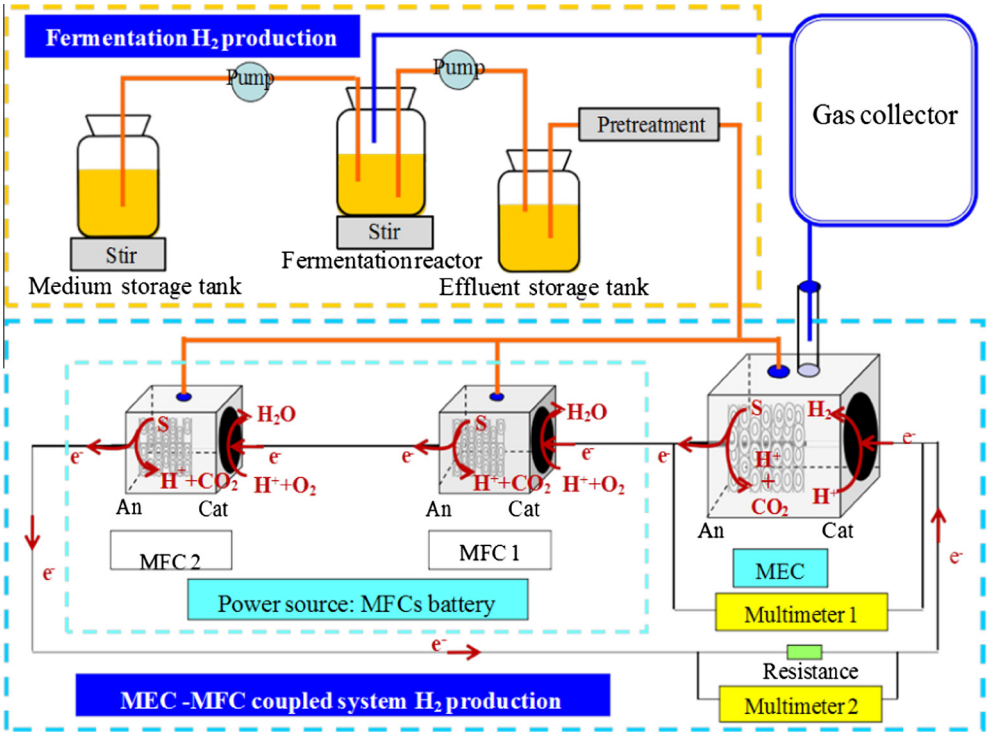

Figure 17 Sketch of the integrated hydrogen production process consisting of fermentation, an MEC and MFCs (S: substrates; An: anode electrode; Cat: cathode electrode).

overall systemic CE were 88–96% and 28–33%, respectively, and the overall systemic hydrogen yield (Y_{sysH2}) peaked at 1.21 mol-H_2 mol-acetate^{-1}. In order to improve the voltage supply, one or two additional MFCs were introduced into the MFC–MEC coupled system [53]. The hydrogen production was significantly enhanced by connecting MFCs in series.

3.2. Dark fermentation and MFC–MEC coupled system for H_2 production

The integrated hydrogen production system consisted of a dark fermentation reactor, one to three MFCs, and one MEC (Fig. 17).

Cellulose was continuously fed to the fermentation reactor, with the effluent collected and used as described below for feeding the MFCs and MECs. Two MFCs (each 25 mL) connected in series to an MEC (72 mL) produced a maximum of 0.43 V using fermentation effluent as a feed, achieving a HPR from the MEC of 0.48 m^3 $H_2/m^3/d$ (based on the MEC volume), and a yield of 33.2 mmol H_2/g COD removed in the MEC [54].

3.3. Dye-sensitized solar cell (DSSC)-powered MEC

A dye sensitized solar cell (DSSC) has been used to provide an additional reductive power from light to an MEC. H-shaped two-chambered glass bottle MECs were run with the assistance of DSSCs as an external power source. The coupled system was tested for hydrogen production (Fig. 18).

An open circuit voltage of 0.6 V was produced by the DSSC and then supplied to the MEC. The whole system produced 400 mmol H_2 within 5 h with cathode recovery efficiency of 78% [55]. In order to further reduce the cost of this coupled system, the platinum catalyst-free cathode of MEC was developed [56]. 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, significant enhancement in hydrogen production

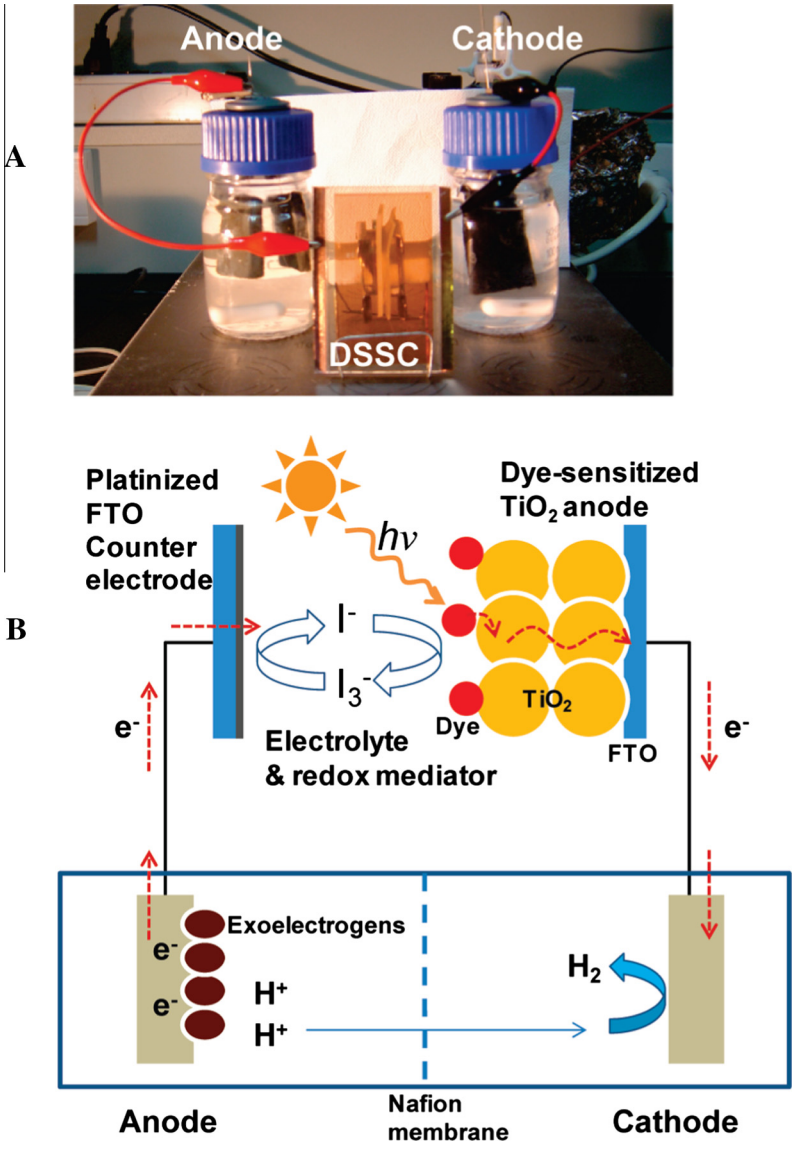

Figure 18 Solar-powered MEC for hydrogen production. (A) Photograph. (B) Schematic diagram.

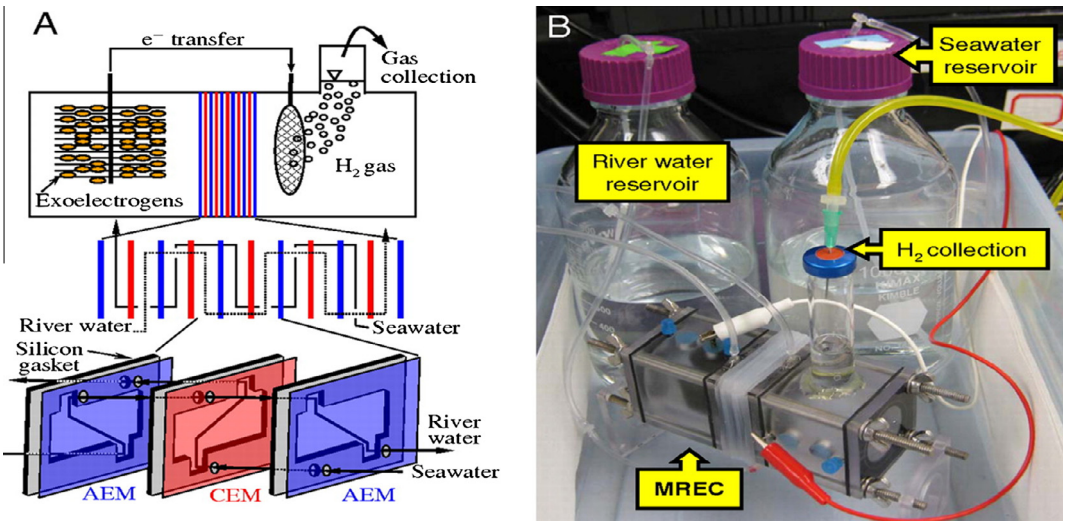

Figure 19 (A) Schematic design of MREC for H_2 production by integrating exoelectrogens with five-cell paired RED stack. (B) Continuous flow and H_2 collection for MREC operation.

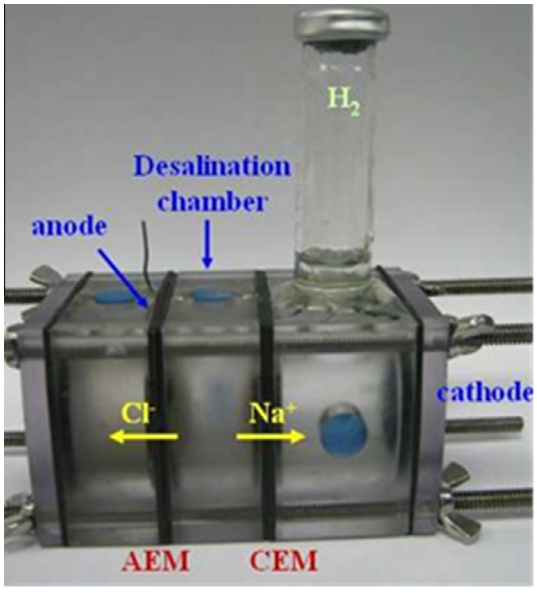

Figure 20 Picture of the three-chamber MDEC.

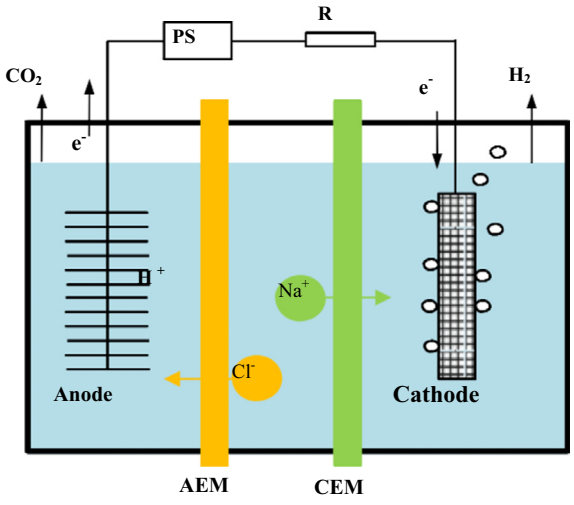

Figure 21 Schematic diagram of the MEDC system.

was observed using carbon nanopowder-coated electrode without Pt [56]. 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.

3.4. Microbial reverse-electrodialysis electrolysis cells (MRECs)

Kim and Logan [57] developed a unique method for hydrogen production based on combining a small reverse electrodialysis stack (five membrane pairs) into a MEC, and renamed it as MREC [57]. 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. The MREC, constructed with five pairs of seawater and river water cells, produced from 21 to 0.026 L of gas over each fed-batch cycle. A cubic Lexan block with a cylindrical chamber (0.03 L, 7 cm^2 in cross section) was used for an anode and cathode container, with a glass tube (0.02 L) glued to the top of the cathode chamber to collect H_2. Only five pairs of seawater and river water cells were sandwiched between an anode, containing exoelectrogenic bacteria, and a cathode, forming a MREC (Fig. 19).

Exoelectrogens added an electrical potential from acetate oxidation and reduced the anode overpotential, while the reverse electrodialysis stack contributed 0.5–0.6 V at a salinity ratio (seawater:river-water) of 50. The HPR increased from 0.8 to 1.6 m^3-H_2/m^3-anolyte/day for seawater and river water flow rates ranging from 0.1 to 0.8 mL/min. H_2 recovery, the ratio of electrons used for H_2 evolution to electrons released by substrate oxidation, ranged from 72% to 86%. Energy efficiencies, calculated from changes in salinities and the loss of organic matter, were from 58% to 64%.

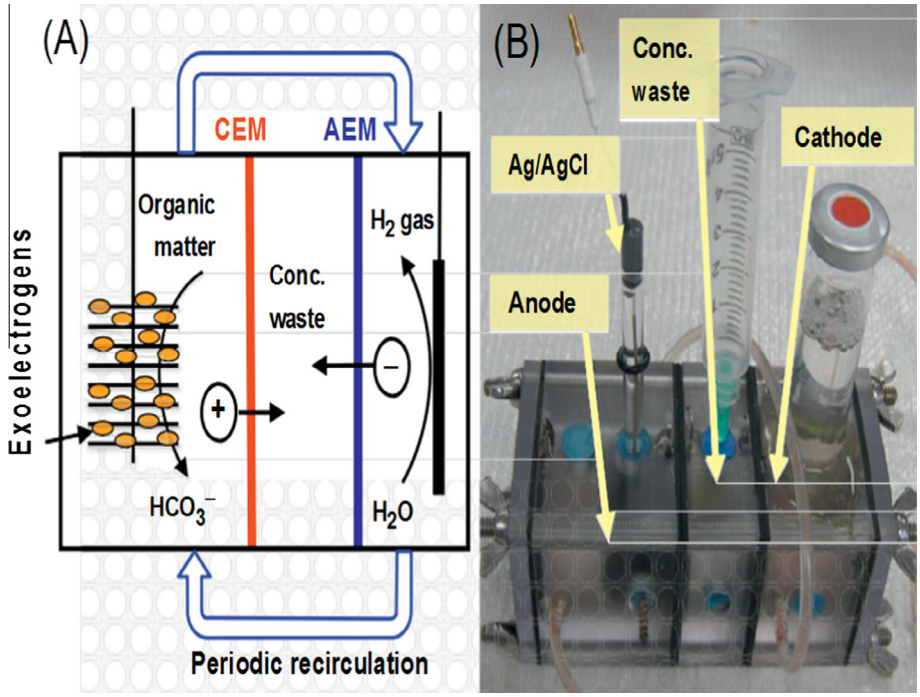

Figure 22 (A) Schematic design of three-chamber MSC for simultaneous removal of organic matter and salt ions, and (B) photograph of the constructed MSC.

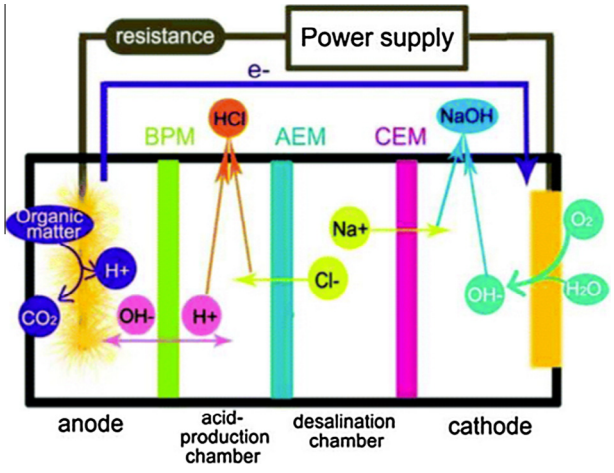

Figure 23 Schematic design of MEDCC for desalination as well as acid and alkali productions.

3.5. Microbial electrodialysis cell (MEDC)

MECs have been integrated with microbial desalination cell (MDC) to boost the desalination performance and energy recovery. Mehanna et al. [58] for the first time demonstrated the integration of MEC with MDC, and the new system was renamed as microbial electrodialysis cell (MEDC) (Fig. 20).

In this experiment, two different initial NaCl concentrations of 5 g/L and 20 g/L were examined. Conductivity in the desalination chamber was reduced by up to 68 ± 3% in a single fed-batch cycle, with electrical energy efficiencies reaching 231 ± 59%, and maximum hydrogen production rates of 0.16 ± 0.05 m^3 H_2/m^3 d obtained at an applied voltage of 0.55 V. Compared to the previous study, much higher HPR 1.5 m^3 $H_2/m^3/d$ (1.6 mL/h) from cathode chamber was obtained due to the relatively higher voltage added (0.8 V). Correspondingly, 98.8% removal of the 10 g/L NaCl was observed [59] (Fig. 21).

3.6. Microbial saline-wastewater electrolysis cell (MSC)

The MEDC was further modified by exchanging the position of AEM and CEM and renamed as MSC [59]. In an MSC, electroactive biofilm on the anode degrades organic matters in saline wastewater, and hydrogen is produced at the cathode as what is done in an MEDC or MEC (Fig. 22).

Unlike MEDC, MSC can simultaneously remove 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 [59].

3.7. Microbial electrolysis desalination and chemical production cell (MEDCC)

By combining the microbial electrolysis cell and the microbial desalination cell (MDC), the microbial electrolysis desalination cell (MEDC) becomes a novel device to desalinate salty water. The desalination process in these systems results in large pH differences in anode (pH decrease) and cathode (pH increase) chambers [60]. The low pH (< 5) in the anode chamber is harmful to the microbial activities, while the high pH in the cathode lowers the hydrogen production rate. Secondly, high levels of Cl^- accumulated in the anode chamber may also inhibit the microbial activities [58,61]. To solve these problems, Chen et al. [61] developed a microbial electrolysis desalination

and chemical-production cell (MEDCC) with four chambers using a bipolar membrane (Fig. 23).

With applied voltages of 0.3–1.0 V, 62–97% of CE were achieved from the MEDCC, which were 1.5–2.0 times of those from the MEDC. With 10 mL of 10 g/L NaCl in the desalination chamber, desalination rates of the MEDCC reached 46–86% within 18 h.

4. Conclusions

This review summarizes the various MEC reactors that have been developed for sustainable and high yield hydrogen gas production as well as waste treatment. There have been many types of MEC rectors developed since the discovery of this technology in 2005 [16,17].

Most of the studies were done in two chamber reactors with a membrane. The main reason behind this was to avoid hydrogen leaking into the anode chamber where it could potentially be used by hydrogenotrophic microorganisms. A membrane also kept the hydrogen production separate from the carbon dioxide produced at the anode therefore ensuring higher hydrogen gas purity at the cathode. However, Rozendal et al. [19] showed that the presence of a membrane led to a high pH gradient across the membrane. Also a major disadvantage of the MEC with membranes is the cost of the membrane can be quite high [18,41].

It has recently shown that membrane-free MEC designs can lead to both high hydrogen recoveries and production rates. Since then multiple studies have developed reactors that operate without membranes. Membrane-free operation removes the associated pH gradient and potential losses and reduces the internal resistance of the system, which in turn allows for more of the applied voltage to be invested in driving the electrode reactions. However, the trade-off is that both carbon dioxide and methane (as low as 1%) will be present in the collected gas if a mixed culture is used. This occurs due to the presence of microorganisms within mixed cultures that consume hydrogen and reduce carbon dioxide for the production of methane. These methanogens are typically slow growing organisms that are sensitive to oxygen, and intermittent air exposure and short retention times can help reduce methane generation, but do not completely eliminate it. Pilot-scale continuous flow microbial electrolysis cells have been developed recently. However, these designs had large internal resistances due to the distance between electrodes and the diffusion resistance of ions through the membranes. Removing membrane separators and increasing the solution conductivity reduce internal resistance, allowing for higher HPR.

It is hoped that in coming years, with the expected improvement in MECs reactor design and lower costs, more scalable MEC designs will be used leading to sustainable and economical hydrogen energy. These improved systems will be able to produce hydrogen gas from almost any renewable material including wastes and plant based biomass.

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References

[1] S. Ritter, Green solutions to global problems, Sci. Technol. 12 (2003) 31–33.
[2] International Energy Agency (IEA), International Energy Outlook, 2014. <www.eia.gov/forecasts/ieo/index.cfm> (accessed 15.07.15).
[3] S. Cheng, B.E. Logan, High hydrogen production rate of microbial electrolysis cell (MEC) with reduced electrode spacing, Bioresour. Technol. 102 (2011) 3571–3574.
[4] C. Ramos, G. Buitron, I. Moreno-Andrade, R. Chamy, Effect of initial total solids concentration and initial pH on the biohydrogen production from cafeteria food waste, Int. J. Hydrogen Energy 37 (2012) 13288–13295.
[5] G. Kumar, C.Y. Lin, Bioconversion of de-oiled Jatropha waste to hydrogen and methane: influence of substrate concentration, temperature and pH, Int. J. Hydrogen Energy 38 (2013) 63–72.
[6] C. Hernandez-Mendoza, G. Buitron, Suppression of methanogenic activity in anaerobic granular biomass for hydrogen production, J. Chem. Technol. Biotechnol. 89 (2013) 143–149.
[7] L. Schlapbach, A. Züttel, Hydrogen-storage materials for mobile applications, Nature 414 (2001) 353–358.
[8] C.Y. Lin, C.H. Lay, C.Y. Chu, B. Sen, G. Kumar, C.C. Chen, Fermentative hydrogen production from wastewaters: a review and prognosis, Int. J. Hydrogen Energy 37 (2012) 15632–15642.
[9] G. Kumar, C.Y. Lin, Biogenic hydrogen conversion of de-oiled Jatropha waste (DJW) via anaerobic sequencing batch reactor operation: process performance, microbial insights and CO_2 reduction efficiency, Sci. World J. 2014 (2014) 1–9.
[10] X.M. Guo, E. Trably, E. Latrille, H. Carrere, J.P. Steyer, Hydrogen production from agricultural waste by dark fermentation: a review, Int. J. Hydrogen Energy 35 (2010) 10660–10673.
[11] Z. Lai, M. Zhu, X. Yang, J. Wang, S. Li, Optimization of key factors affecting hydrogen production from sugarcane bagasse by a thermophilic anaerobic pure culture, Biotechnol. Biofuels 7 (2014) 1–11.
[12] I.P. Jain, Hydrogen the fuel for 21st century, Int. J. Hydrogen Energy 34 (2009) 7368–7378.
[13] C. Acar, I. Dincer, Comparative assessment of hydrogen production methods from renewable and non-renewable sources, Int. J. Hydrogen Energy 39 (2014) 1–12.
[14] B.E. Logan, D. Call, S. Cheng, H.V. Hamelers, T.H. Sleutels, A. W. Jeremiasse, Microbial electrolysis cells for high yield hydrogen gas production from organic matter, Environ. Sci. Technol. 42 (2008) 8630–8640.
[15] U.S. Meda, S.S.N. Rakesh, M.A.L.A. Raj, Bio-hydrogen production in microbial electrolysis cell using waste water from sugar industry, Int. J. Eng. Sci. Res. Technol. 4 (2015) 452–458.
[16] H. Liu, S. Grot, B.E. Logan, Electrochemically assisted microbial production of hydrogen from acetate, Environ. Sci. Technol. 39 (2005) 4317–4320.
[17] R.A. Rozendal, C.J.N. Buisman, Process for Producing Hydrogen, Patent WO2005005981, 2005.
[18] D. Call, B.E. Logan, Hydrogen production in a single chamber microbial electrolysis cell (MEC) lacking a membrane, Environ. Sci. Technol. 42 (2008) 3401–3406.
[19] R.A. Rozendal, H.V.M. Hamelers, R.J. Molenkamp, C.J.N. Buisman, Performance of single chamber biocatalyzed

electrolysis with different types of ion exchange membranes, Water Res. 41 (2007) 1984–1994.
[20] H. Liu, H. Hu, J. Chignell, Y. Fan, Microbial electrolysis: novel technology for hydrogen production from biomass, Biofuels 1 (2010) 129–142.
[21] A. Kundu, J.N. Sahu, G. Redzwan, M.A. Hashim, An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell, Int. J. Hydrogen Energy 38 (2013) 1745–1757.
[22] M. Zhou, H. Wang, D.J. Hassett, T. Gu, Recent advances in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) for wastewater treatment, bioenergy and bioproducts, J. Chem. Technol. Biotechnol. 88 (2013) 508–518.
[23] A. Kadier, Y. Simayi, M.S. Kalil, P. Abdeshahian, A.A. Hamid, A review of the substrates used in microbial electrolysis cells (MECs) for producing sustainable and clean hydrogen gas, Renew. Energy 71 (2014) 466–472.
[24] R.A. Rozendal, H.V. Hamelers, K. Rabaey, J. Keller, C.J. Buisman, Towards practical implementation of bioelectrochemical wastewater treatment, Trends Biotechnol. 26 (2008) 450–459.
[25] Y. Zhang, I. Angelidaki, Microbial electrolysis cells turning to be versatile technology: recent advances and future challenges, Water Res. 56 (2014) 11–25.
[26] T. Jafary, W.R.W. Daud, M. Ghasemi, B.H. Kim, J. MdJahim, M. Ismail, S.S. Lim, Biocathode in microbial electrolysis cell; present status and future prospects, Renew. Sustain. Energy Rev. 47 (2015) 23–33.
[27] B.H. Kim, S.S. Lim, W.R.W. Daud, G.M. Gadd, I.S. Chang, The biocathode of microbial electrochemical systems and microbially-influenced corrosion, Bioresour. Technol. 190 (2015) 395–401.
[28] S.M. Daud, B.H. Kim, M. Ghasemi, W.R.W. Daud, Separators used in microbial electrochemical technologies: current status and future prospects, Bioresour. Technol. 195 (2015) 170–179.
[29] V.G. Dababov, Electricity from microorganisms, Mikrobiologiya 77 (2008) 149–157.
[30] P.A. Selembo, M.D. Merrill, B.E. Logan, The use of stainless steel and nickel alloys as low-cost cathodes in microbial electrolysis cells, J. Power Sources 190 (2009) 271–278.
[31] R.A. Rozendal, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, C.J.N. Buisman, Principle and perspectives of hydrogen production through biocatalyzed electrolysis, Int. J. Hydrogen Energy 31 (2006) 1632–1640.
[32] S. Cheng, B.E. Logan, Sustainable and efficient biohydrogen production via electrohydrogenesis, Proc. Natl. Acad. Sci. USA 104 (2007) 18871–18873.
[33] R.A. Rozendal, A.W. Jeremiasse, H.V.M. Hamelers, Effect of the type of ion exchange membrane on performance ion transport and pH in biocatalyzed electrolysis of wastewater, Water Sci. Technol. 57 (2008) 1757–1762.
[34] J.R. Kim, S. Cheng, S.E. Oh, B.E. Logan, Power generation using different cation, anion and ultrafiltration membranes in microbial fuel cells, Environ. Sci. Technol. 41 (2007) 1004–1009.
[35] S. Cheng, B.E. Logan, Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells, Electrochem. Commun. 9 (2007) 492–496.
[36] S. Cheng, H. Liu, B.E. Logan, Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells, Environ. Sci. Technol. 40 (2006) 364–369.
[37] G. Kyazze, A. Popov, R. Dinsdale, S. Esteves, F. Hawkes, G. Premier, A. Guwy, Influence of catholyte pH and temperature on hydrogen production from acetate using a two chamber concentric tubular microbial electrolysis cell, Int. J. Hydrogen Energy 35 (2010) 7716–7722.
[38] J.M. Pisciotta, Z. Zaybak, D.F. Call, J.Y. Nam, B.E. Logan, Enrichment of microbial electrolysis cell (MEC) biocathodes from sediment microbial fuel cells (MFCs) bioanodes, Appl. Environ. Microbiol. 78 (2012) 5212–5219.
[39] J. An, H.S. Lee, Implication of endogenous decay current and quantification of soluble microbial products (SMP) in microbial electrolysis cells, RSC Adv. 3 (2013) 14021–14028.
[40] NIST, NIST chemistry webbook, in: US Secretary of Commerce, 2005, pp. 69.
[41] H. Hu, Y. Fan, H. Liu, Hydrogen production using single-chamber membrane-free microbial electrolysis cells, Water Res. 42 (2008) 4172–4178.
[42] K. Guo, X. Tang, Z. Du, H. Li, Hydrogen production from acetate in a cathode-on-top single-chamber microbial electrolysis cell with a mipor cathode, Biochem. Eng. J. 51 (2010) 48–52.
[43] X. Guo, J. Liu, B. Xiao, Bioelectrochemical enhancement of hydrogen and methane production from the anaerobic digestion of sewage sludge in single-chamber membrane-free microbial electrolysis cells, Int. J. Hydrogen Energy 38 (2013) 1342–1347.
[44] H.S. Lee, C.I. Torres, P. Parameswaran, B.E. Rittmann, Fate of H_2 in an upflow single-chamber microbial electrolysis cell using a metal-catalyst-free cathode, Environ. Sci. Technol. 43 (2009) 7971–7976.
[45] H. Hu, Y. Fan, H. Liu, Hydrogen production in single-chamber tubular microbial electrolysis cells using non-precious metal catalysts, Int. J. Hydrogen Energy 34 (2009) 8535–8542.
[46] H. Liu, B.E. Logan, Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane, Environ. Sci. Technol. 38 (2004) 4040–4046.
[47] D.F. Call, B.E. Logan, A method for high throughput bioelectrochemical research based on small scale microbial electrolysis cells, Biosens. Bioelectron. 26 (2011) 4526–4531.
[48] B. Tartakovsky, M.F. Manuel, H. Wang, S.R. Guiot, High rate membrane-less microbial electrolysis cell for continuous hydrogen production, Int. J. Hydrogen Energy 34 (2009) 672–677.
[49] L. Gil-Carrera, A. Escapa, R. Moreno, A. Morán, Reduced energy consumption during low strength domestic wastewater treatment in a semi-pilot tubular microbial electrolysis cell, J. Environ. Manage. 122 (2013) 1–7.
[50] R.D. Cusicka, B. Bryanb, D. Parkerb, M. Merrilla, M. Mehannaa, P.D. Kielya, G. Liuc, B.E. Logan, Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater, Appl. Microbiol. Biotechnol. 89 (2011) 2053–2063.
[51] X. Wang, S. Cheng, Y. Feng, M.D. Merrill, T. Saito, B.E. Logan, Use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells, Environ. Sci. Technol. 43 (2009) 6870–6874.
[52] M. Sun, G.P. Sheng, L. Zhang, C.R. Xia, Z.X. Mu, X.W. Liu, H.L. Wang, H.Q. Yu, R. Qi, T. Yu, M. Yang, An MECMFC-coupled system for biohydrogen production from acetate, Environ. Sci. Technol. 42 (2008) 8095–8100.
[53] M. Sun, G.P. Sheng, Z.X. Mu, X.W. Liu, Y.Z. Chen, H.L. Wang, H.Q. Yu, Manipulating the hydrogen production from acetate in a microbial electrolysis cell microbial fuel cell-coupled system, J. Power Sources 191 (2009) 338–343.
[54] A. Wang, D. Sun, G. Cao, H. Wang, N. Ren, W.M. Wu, B.E. Logan, Integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cells, and a microbial electrolysis cell, Bioresour. Technol. 102 (2011) 4137–4143.
[55] F.F. Ajayi, K.Y. Kim, K.J. Chae, M.J. Choi, S.Y. Kim, I.S. Chang, I.S. Kim, Study of hydrogen production in light assisted microbial electrolysis cell operated with dye sensitized solar cell, Int. J. Hydrogen Energy 34 (2009) 9297–9304.
[56] K.J.M.J. Chae, K.Y. Choi, F.F. Ajayi, I.S. Chang, I.S. Kim, A solar-powered microbial electrolysis cell with a platinum

catalyst-free cathode to produce hydrogen, Environ. Sci. Technol. 43 (2009) 9525–9530.
[57] Y. Kim, B.E. Logan, Hydrogen production from inexhaustible supplies of fresh and salt water using microbial reverse-electrodialysis electrolysis cells, Proc. Nat. Acad. Sci. 108 (2011) 16176–16181.
[58] M. Mehanna, P.D. Kiely, D.F. Call, B.E. Logan, Microbial electrodialysis cell for simultaneous water desalination and hydrogen gas production, Environ. Sci. Technol. 44 (2010) 9578–9583.
[59] Y. Kim, B.E. Logan, Simultaneous removal of organic matter and salt ions from saline wastewater in bioelectrochemical systems, Desalination 308 (2013) (2013) 115–121.
[60] H. Luo, P.E. Jenkins, Z. Ren, Concurrent desalination and hydrogen generation using microbial electrolysis and desalination cells, Environ. Sci. Technol. 45 (2011) 340–344.
[61] S. Chen, G. Liu, R. Zhang, B. Qin, Y. Luo, Development of the microbial electrolysis desalination and chemical production cell for desalination as well as acid and alkali productions, Environ. Sci. Technol. 46 (2012) 2467–2472.