Journal of Power Sources 196 (2011) 4427–4435

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review

An overview of electrode materials in microbial fuel cells

Minghua Zhou[a,*], Meiling Chi[a], Jianmei Luo[b], Huanhuan He[a], Tao Jin[a]

[a] Key Laboratory of Pollution Processes and Environmental Criteria of Ministry of Education, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China
[b] Key Laboratory of Industrial Microbiology, Ministry of Education, College of Biotechnology, Tianjin University of Science and Technology, Tianjin 300457, China

ARTICLE INFO

Article history:
Received 17 December 2010
Accepted 4 January 2011
Available online 14 January 2011

Keywords:
Microbial fuel cells
Electrode materials
Modification and characterization
Wastewater treatment

ABSTRACT

Electrode materials play an important role in the performance (e.g., power output) and cost of microbial fuel cells (MFCs), which use bacteria as the catalysts to oxidize organic (inorganic) matter and convert chemical energy into electricity. In this paper, the recent progress of anode/cathode materials and filling materials as three-dimensional electrodes for MFCs has been systematically reviewed, resulting in comprehensive insights into the characteristics, options, modifications, and evaluations of the electrode materials and their effects on different actual wastewater treatment. Some existing problems of electrode materials in current MFCs are summarized, and outlooks for future development are also suggested.

Contents

1. Introduction

Energy shortage and environmental pollution have brought forth global crises and seriously impacted human survival and development. Microbial fuel cells (MFCs) exactly meet the need to alleviate the above-mentioned crises as they can not only produce

* Corresponding author. Tel.: +86 22 23507800; fax: +86 22 23507800.
E-mail addresses: zhoumh@nankai.edu.cn, skynumen@163.com (M. Zhou).

0378-7753/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2011.01.012

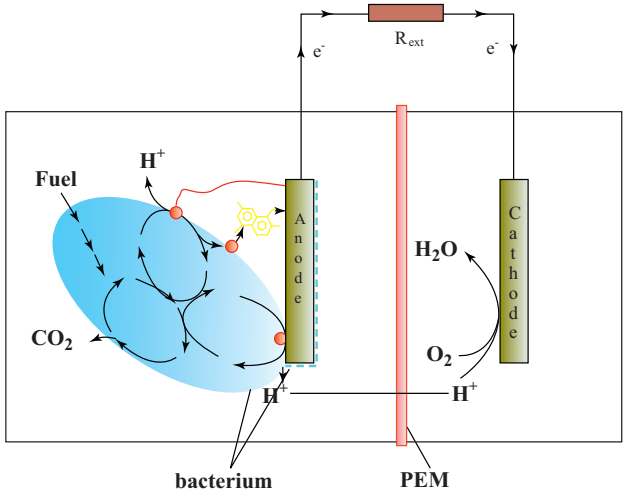

Fig. 1. Schematic diagram of the dual-chamber MFC structure (represents the mediator) [3].

electricity but also have a great potential for simultaneous wastewater treatment [1,2]. They have therefore become one of the major research hotspots in many countries.

MFCs are devices that use bacteria as the catalysts to oxidize organic (inorganic) matter and directly convert chemical energy into electrical energy [3–5]. Traditional MFCs are composed of an anode chamber and a cathode chamber separated by a proton exchange membrane (PEM), as shown in Fig. 1. The substrate in the anode chamber is oxidized by microbial metabolism under anaerobic conditions, producing electrons and protons. After being transferred to the anode by direct membrane-associated electron transfer, electron mediators or nanowires, the electrons flow to the cathode, which is linked by an external circuit. Simultaneously, protons reach the cathode through the PEM. Reduction reaction occurs among the electrons, protons and electron acceptor (e.g., air or oxygen) in the cathode chamber, producing H_2O [6,7]. In this way a continuous current is generated while achieving the removal of pollutants.

The English botanist Potter (1911) first discovered that bacteria inocula could generate current, but this finding was not well appreciated until the 1980s, when the addition of electron mediators substantially improved the output power of MFCs. A real breakthrough was made when some microbes were found that were able to transfer electrons directly to the anode. The number of MFCs applied to the biological treatment of wastewater increase greatly during the 1990s, especially after Logan and other researchers developed new MFCs using municipal or industrial wastewater as the substrate which greatly facilitated the technology [8,9]. At present, however, one of the bottleneck problems for the application of this methodology is the low output of power.

Principally, the output power depends on the rate of substrate degradation, the rate of electron transfer from the bacteria to the anode, the circuit resistance, the proton mass transfer in the liquid [10], the performance of the electrode and the external operating conditions and so on. Different electrode materials vary in their physical and chemical properties (e.g., surface area, electric conductivity, and chemical stability), thus, they also vary in their impact on microbial attachment, electron transfer, electrode resistance and the rate of electrode surface reaction. Therefore, it is of great significance to select and develop suitable electrode materials to optimize and promote the performance of MFCs. Moreover, as a main component, the electrode materials determine the price of MFCs and thus influence the wastewater treatment cost. Therefore, this field has attracted ever-increasing interest and lots of efforts related to electrode preparations and designs have been made. Unfortunately, to the best of our knowledge, there are almost no comprehensive reports on the review of electrode materials in MFCs. In this paper, a systematical review of the electrode fabrication, modification, evaluation, characteristics and application for typical wastewater treatment was summarized. Some existing problems of electrode materials in current MFCs were disclosed, and outlooks for future development were also suggested, which would help to gain knowledge and contribute to the development of MFCs and their application in wastewater treatment.

2. Electrode materials used in MFCs

So far, electrode materials in MFCs can be principally divided into three categories: anode, cathode, and filling materials as three-dimensional electrodes.

2.1. Anode materials

A good anode material should have the following properties [3]: (a) good electrical conductivity and low resistance; (b) strong biocompatibility; (c) chemical stability and anti-corrosion; (d) large surface area; and (e) appropriate mechanical strength and toughness.

2.1.1. Traditional carbon anode materials

Carbon materials are the most widely used anodes in the present MFCs studies; they traditionally including graphite rod, graphite fiber brush, carbon cloth, carbon paper, carbon felt, and reticulated vitreous carbon (RVC), as is shown in Fig. 2. Table 1 lists their characteristics and some references in which they have been utilized.

Due to its excellent electrical conductivity and chemical stability, the graphite rod has become one of the most commonly used electrodes in MFCs. The most representative work was done by Liu et al. [6], in which a single-chamber MFC included eight graphite rod anodes and an air cathode was developed (Fig. 2A). A maximum power of 26 mW m^{-2} and 80% COD removal were fulfilled, using sewage from the primary sedimentation tank of a treatment plant as fuel. However the application of the graphite rod was limited because of its low porosity and surface area for microorganism adsorption. Lovley and his co-workers found that the output power was much larger when the graphite rod was replaced instead by graphite felt, indicating that increasing the surface area was beneficial to the performance of the MFC [11].

A graphite fiber brush is made of graphite fiber that is wound around one or more conductive corrosion-resistant metal wires (titanium wire) (Fig. 2B); it is attractive for its high surface area and low electrode resistance. Ahn and Logan [12] designed a single-chamber air-cathode MFC with a continuous flow that used a graphite brush as the anode, acquiring a maximum power density of 422 mW m^{-2}. In another work, a flat-type MFC with a graphite brush as the anode and a 1.2 mg cm^{-2} cobalt tetramethylphenylporphyrin (CoTMPP) carbon cloth as the cathode, a power density of up to 2400 mW m^{-2} was obtained, which was four times that obtained when using carbon paper as the anode (600 mW m^{-2}) [13].

Carbon paper and carbon cloth, which are often applied in the hydrogen fuel cells, are now used in MFCs as flat-plate electrodes. These kinds of electrodes benefit from a reduction in the distance between the two electrodes to improve the performance of the MFCs. Kim et al. [14] constructed a dual-chamber MFC with carbon paper, and the power density was up to 40 mW m^{-2}. Wang et al. [15] built a single-chamber MFC that used carbon cloth as the electrode and actual brewery wastewater as the anode substrate, and the maximum power density was 483 mW m^{-2}.

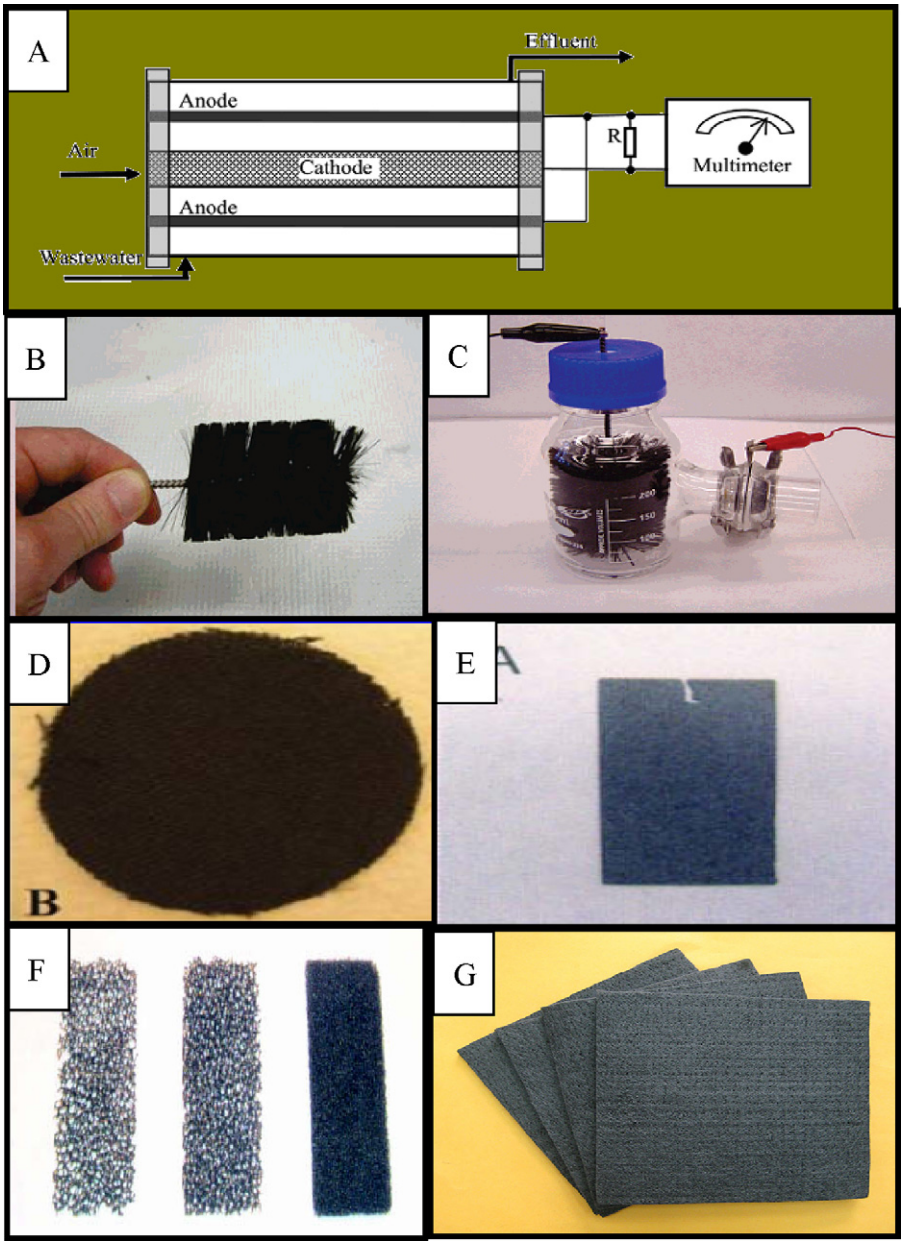

Fig. 2. Anode materials used in MFCs: (A) graphite rod anode in a single-chamber MFC [4]; (B) graphite brush [13]; (C) graphite brush anode in a single-chamber MFC [13]; (D) carbon cloth [16]; (E) carbon paper anode in dual-chamber MFC [66]; (F) RVC [66]; and (G) carbon felt [67].

Compared with the carbon materials described above, reticulated vitreous carbon (RVC) is less frequently used in MFCs studies due to its large resistance. He et al. obtained a power density of 170 mW m^{-2} in an upflow MFC using RVC as the anode material [9].

In addition to the electrode materials described above, other carbon-like materials have emerged in recent MFC studies. Wang et al. [16] attempted to use carbon mesh, which is cheaper than using carbon cloth as the anode in MFCs, and the power density increased to 1015 mW m^{-2} (51 W m^{-3}). A new type of filler-type anode with carbon felt and carbon paper using the sintering method was developed by Liang et al. [17], achieving an extremely high power density of 2426 mW m^{-2}. This result was explained by the fact that the sintered filler-type anode could enhance the connection between the fillers and the carbon paper, reducing the anode resistance.

Table 1
Comparison of the characteristics of traditional anode materials in MFCs.

Anode materials	Advantages	Disadvantages	Literature
Graphite rod	Good electrical conductivity and chemical stability, relatively cheap, and easy to get	Difficult to increase the surface area	[10]
Graphite fiber brush	Higher specific surface areas, easy to produce	Clogging	[12]
Carbon cloth	Large relative porosity	Expensive	[68]
Carbon paper	Easy to connect wiring	Lack of durability, fragile	[14]
Carbon felt	Large aperture	Large resistance	[69]
RVC	Good electrical conductivity and plasticity	Large resistance, fragile	[9]

Table 2
The performance of anode with carbon nanotubes and conductive polymer in MFCs.

Anode materials	MFC construction	Bacteria	Substrate	Electron acceptor	Preparation method	Cell voltage (mV)	P_{max} (mW m^{-2})	I_{max} (mA m^{-2})	Reference
CNT/polyaniline composite	–	*E. coli*	Glucose	–	In situ via chemical oxidation	450	42	100	[18]
Carbon paper with Sn–Pt/MWNT	DCMFC	*E. coli*	Glucose	Hexacyanoferrate	Chemical vapor deposition	~400	2470	~6000	[19]
Carbon paper with PPy-CNTs	DCMFC	*E. coli*	Glucose	Ferricyanide	In situ chemical polymerization	180	228	1278	[20]
Carbon cloth with CNTs	SCMFC	Mixed bacteria	Sodium acetate	Air	Chemical vapor deposition	200	65	~300	[21]
Carbon nanotubes	SCMFC	Mixed bacteria	Sodium acetate	Air	Vapor deposition	–	402	–	[70]

SCMFC: single-chamber MFC; DCMFC: double-chamber MFC.

2.1.2. Carbon nanotubes (CNTs) and conductive polymer

Since their discovery, CNTs have become one of the electrode materials with the most potential because of their large specific surface area, high mechanical strength and ductility, and excellent stability and conductivity. Recently, conductive polymer/CNTs composites have received significant interest because the incorporation of CNTs in conductive polymers can lead to a synergistic effect.

Table 2 summaries some typical studies that have used CNTs and/or conductive polymer as the anode. Qiao et al. [18] reported the feasibility of an MFC that used CNTs/polyaniline composite as the anode material. They believed that CNTs could enhance the electrode surface area and electron transfer capability. Additionally, polyaniline, as a conductive polymer, could not only provide a protective effect for the microorganisms but also improve the electro-catalytic activity of the catalyst. Sharma et al. [19] developed MFC using an anode of carbon paper that was deposited with multi-walled CNTs; to their great surprise, the power density was found to be approximately six times greater than that found with of the pure graphite electrode. They confirmed that the carboxyl groups on the surface of multi-walled CNTs could increase the chemical reactivity of metal nanoparticles. Zou et al. [20] used polypyrrole (PPy)/CNTs as the anode material, and the results showed that the modified carbon paper had better electrochemical properties. Tsai et al. [21] considered that the modified electrode could improve the performance of MFCs; when compared to the unmodified electrode, the power density and cell voltage increased by approximately 148% and 147%, respectively.

There is no question that CNTs can improve the performance of MFCs because they have very high surface areas (usually a few hundred to 1300 m^2 g^{-1}), and the groove openings that are formed between CNTs bundles and the outside surface area of CNTs bundles are supposed to be accessible by large sorbate species such as bacteria, which makes the increased surface area effective for microscale bacteria and significantly larger than that of traditional microporous adsorbent media [22,23]. However, there are still some clogging issues that have hindered the application of CNTs for wastewater treatment at present. First of all, the high cost of CNTs manufacture, which was reported to be $80–100 is one of the major factors [24,25]. Secondly, the fabrication of CNTs is complex and expensive, which also limits their large-scale commercial production [26]. The present synthesis techniques, including arc discharge, laser ablation and chemical vapor decomposition (CVD), either limit the volume of the sample, need subsequent purification steps to separate the CNTs from undesirable by-products [27] or produce nanotubes with defects. However, we may expect that the application would be intensified with the reduction of the cost of CNTs and the increase in commercial production capacity in the near future [28].

2.1.3. Non-carbon anode materials

In the study of MFCs, carbon-based materials are generally regarded as the most versatile anodes although several reports have attempted to use non-carbon materials. Dumas et al. [29] attempted sediment MFC using stainless steel as the electrode, but the maximum power density was only 4 mW m^{-2}. Richter et al. [30] developed an MFC using highly conductive gold as the anode with Geobacter sulfurreducens, and a steady current of 0.4–0.7 mA was produced. Although this MFC can obtain a power that is similar to the graphite electrode, its practical application is limited to the small scale. Heijne et al. [31] tried to use titanium as the anode, but they found that it was unsuitable.

2.2. Cathode materials

The cathode materials also have a great impact on the power capacity of MFCs, which should have a high redox potential and

Table 3
Non-Pt catalysts of cathode in MFCs.

Type of catalyst	Cathode materials	OCP (V)	P_{max} (mW m^{-2})	Reference
CoTMPP	Carbon cloth	–	369	[33]
PbO_2	Ti sheeting	–	78	[34]
FePc	Carbon paper	0.319	634	[57]
FePcVC		0.289	530	
CoTMPP		0.325	483	
MnPc		0.285	353	
FePc	Graphite foils	1.07	13.88*	[71]
CoTMPP		1.10	14.32*	
Rutile	Graphite plate	0.55	–	[72]
PbO_2	Ti sheeting	–	485	[73]
β-MnO_2	Carbon cloth	0.565	3.773*	[74]
Co-OMS-2	Carbon cloth	0.147	180	[75]
MnO_x	Carbon cloth	0.714	161	[76]
Co/Fe/N/CNT	Carbon cloth	0.473	751	[77]

*W m^{-3}.

easily to capture protons. Presently, the common cathode materials are graphite, carbon cloth and carbon paper.

To improve performance, modifying the cathode with a highly active catalyst, e.g., Pt, which has been the most popular one to try [5], is supposed to reduce the cathodic reaction activation energy and increase the reaction rate. Moon et al. [32] designed an MFC that used graphite felt containing Pt as the cathode, and its power density reached 150 mW m^{-2}, which was three times higher than that for the pure graphite cathode.

However, Pt is an expensive metal and this limits its practical application. Many efforts have been made to reduce cathode costs by decreasing Pt loading or seeking other non-Pt catalysts. Cheng et al. [33] found that the potential did not change noticeably (maximum of 19%) when the Pt loading on the cathode ranged from 0.1 to 2 mg cm^{-2}. This finding resulted in the Pt modified cathode still being competitive and cost-effective.

Table 3 lists some representative efforts to use non-Pt catalysts. The CoTMPP and iron phthalocyanine (FePc) based oxygen reduction catalysts were investigated more often, and they were proved to be inexpensive and efficient alternatives for MFCs application. Manganese oxides and rutile were also studied. Morris et al. [34] compared PbO_2 to Pt as a cathode catalyst in a double-chamber MFC utilizing glucose as a substrate. The results indicated that the PbO_2 cathode produced 2–4 times more power than that did the Pt cathode. This study suggested that PbO_2 could replace Pt as the cathode catalyst to improve the feasibility of scaling up MFCs for practical applications by enhancing the power generation and decreasing the production cost.

However, the long-term (e.g., more than 1 year) stability of the electrode materials, which is very important for their application, has not attracted considerable attention. Also, because many operational parameters, such as microbial growth, pH and temperature, simultaneously affect the power generation, it is not easy to clearly study why electrode performance varies. Cheng et al. [33] operated MFCs in a fed batch mode over 800 h, and it seemed that power generation was slightly decreased. The maximum power density for the PTFE cathode with Pt decreased by only 9%, or from 360 to 331 mW m^{-2}. When the PTFE was used as the Pt (0.5 mg cm^{-2}) binder on the cathode, the maximum voltage for each cycle did not decrease sharply. The Coulombic efficiency also varied over a small range during the same period from 9.5% to 13.1%.

2.3. Three-dimensional electrode materials

Increasing the electrode surface area is an effective way to improve the performance of MFCs because it enhances the microbe attachment and the bio-electron transfer area. However, in a conventional two-dimensional electrode system, the increase in the electrode size is accompanied by an increase in the reactor volume and the infrastructure costs. The use of inexpensive three-dimensional electrodes, e.g., certain small particle conductive materials, to fill into the chamber may offer one solution.

The graphite particle is perhaps the most commonly used filling material in the anode chamber in a three-dimensional cell. You et al. [7] built a tube-type air cathode MFC that made graphite granules as the anode, and a graphite rod was used to collect electrons, achieving a maximum power density of 50.2 W m^{-3} when using glucose as the substrate. Aelterman et al. [35] constructed six MFCs with an anode of graphite particles and a cathode of graphite rods, and the maximum total power density was 258 W m^{-3} using artificial sodium acetate and potassium ferricyanide as the substrate.

Granular activated carbon (GAC), a commonly used packing material in wastewater treatment processes, is an inexpensive and durable material with a high surface area that could greatly improve bacterial adhesion and might be used as a suitable anode material in MFCs. Jiang and Li [36] utilized GAC as the anode, attaining a power density that exhibited a significant increase from 4.2 to 7.2 W m^{-3} when the amount of GAC increased from 400 to 700 g. This result indicated that the power generation of MFCs increased with the introduction of more GAC due to a higher amount of attached biomass.

Three-dimensional electrodes can support an increased attachment of bacteria and increase the volumetric power density, which should in theory result in the better performance of the MFC reactor. However, at present some challenges that are associated with three-dimensional electrodes need further investigation. Firstly, the efficiency and mechanism of electron transportation are still unclear. In the three-dimensional electrode MFCs, graphite rods are more often used to collect the electrons. But how to ensure the effective transmission of electrons and protons is becoming the most important issue. Secondly, it seems unnecessary to overcome certain disadvantages and adverse effects when three-dimensional electrodes are introduced into MFCs. For example, one study found that the ohmic loss of an MFC with 2 mm granules was almost double that of the average ohmic losses of the other MFCs [37]. And they also found that graphite and carbon felts could be clogged when using wastewaters containing colloids or suspended particles. In addition, the exploration of sound three-dimensional electrode materials and their construction is still a key problem in improving the performance of MFCs.

3. Modification, evaluation and measurement of electrode materials

3.1. Modification of anode materials

The modification of electrode materials proved to be an effective way to improve the performance of MFCs because it changed the physical and chemical properties to provide for better microbial attachment and electron transfer. This section will focus on some conventional modification techniques for anode materials as the modification of the cathode mainly involves changes in the catalysts, which was well described in Section 2.2. In summary, many anode modification methods required complicated apparatuses, multiple steps, high temperature conditions and/or long treatment time. Therefore, more simple or effective modification techniques are still in great and urgent demand; hopefully, this will be a research hotspot for MFCs.

3.1.1. Ammonia treatment

This method is suitable for many carbon electrode materials including carbon cloth and carbon paper, and it has been regarded as one of the most effective ways to improve electrode perfor-

Table 4
Modified electrode materials and methods.

Chemically modified anode	Modified methods	OCP (mV)	P_{max} (mW m^{-2})	I_{max} (mA cm^{-2})	Reference
Mn^{4+}-graphite	Soak method	–	788	1.75	[39]
Ferric oxide	Chemical vapor deposition technique	–	30	–	[40]
Tungsten carbide	High temperature carburization	–	–	8.8	[41]
Graphite/ceramic-Mn^{2+}–Ni^{2+}	Sintering process	−318	~105	–	[42]
Graphite/Fe_3O_4	Sintering process	−400	–	–	
Graphite/Fe_3O_4–Ni^{2+}	Sintering process	−472	–	–	
Graphite/AQDS	Soak method	−403	~98	–	
Graphite/NQ	Soak method	−411	–	–	
Plain graphite	–	−411	~20	–	

mance [16,38]. The first report using ammonia to treat carbon cloth was completed by Cheng and Logan [38]. The modification process was as follows: after gradient heating up to 700 °C using a thermo-gravimetric analyzer (TGA) under a nitrogen environment, the carbon cloth was placed for 60 min in He containing 5% NH_3; then, it was cooled down to room temperature after 120 min in the N_2 environment. They concluded that the acclimation time after ammonia treatment was 2/5 less than the untreated one, while the maximum power density was increased by 48%. This result occurred mainly because the treated carbon cloth can improve the amount of surface charge (from 0.38 to 3.99 mequiv. m^{-2}) and thus is more conductive to microbial electron transport.

3.1.2. Chemical modification

The chemical modification method is supposed to be effective for immobilizing metals, metal oxides or other active compounds on the carriers, such as carbon materials or conductive polymers, to enhance the output power of MFCs. Table 4 summarizes the performance of some modified electrode materials and their modification methods, including chemical vapor deposition, carburization, sintering or soak method. Park and Zeikus [39] incorporated Mn^{4+} into the anode by the soak method, and the power density was able to reach 788 mW m^{-2}. Kim et al. [40] coated the anode with ferric oxide and observed that the power density increased noticeably from 8 to 30 mW m^{-2} because of the enrichment of metal-reducing bacteria on the anode. Rosenbaum et al. [41] adopted a high-performance tungsten carbide anode that was modified by carburization, which was expected to produce well-coordinated electro-catalysis and bio-catalytic electrolysis at the interface. Lowy et al. [42] studied the performance of MFCs using several kinds of modified electrodes by the sintering process or the soak method. They prepared and discussed using graphite modified with anthraquinone-1,6-disulfonic acid (AQDS), 1,4-naphthoquinone (NQ), a graphite-ceramic composite containing Mn^{2+} and Ni^{2+}, and a graphite paste containing Fe_3O_4 or Fe_3O_4 and Ni^{2+}, observing that some modifications (graphite/ceramic-Mn^{2+}–Ni^{2+}, graphite/AQDS) led to both a considerable change in the open circuit potential (OCP) and a great improvement in the power output (4–5 times that of the unmodified one).

3.1.3. Other modification methods

Other electrode modification methods include heat treatment, acid treatment and so on. The main purposes are to remove impurities of the electrode surface and, more importantly, to increase the active area, conductivity and/or quinone/quinone functional groups on the surface [43].

Wang et al. [9] heated carbon mesh in a muffle furnace at 450 °C for 30 min, which resulted in a maximum power density of 922 mW m^{-2} (46 W m^{-3}); this was 3% more than that produced using a mesh anode that was cleaned with acetone (893 mW m^{-2}; 45 W m^{-3}). They attributed such a change in the power density to the facts that the heating method could modify the electrochemical activity by increasing the electrochemically active surface area and decreasing the O/C ratio, which led to the active surface area increasing by 190% and the charge transfer coefficients increasing by 44% compared to the untreated one.

The acid treatment of an electrode is very simple: the electrode material is placed into an acid solution for a period of time, is then removed and washed with deionized water several times, and finally is dried at a suitable temperature. Erable et al. [44] modified graphite particles with nitric acid in a procedure similar to that described above, and it was found that both the electro-catalytic properties and the oxygen reduction capability were improved. As compared to the untreated version, the cell voltage increased from 660 to 1050 mV. By further analysis by BET and XPS, they concluded that such an improvement in the oxygen reduction reaction (ORR) might be explained by the modification of the BET surface area coupled to the emergence of nitrogen superficial groups on the surface of activated granules.

In certain cases, several modified methods are used concurrently to achieve a better treatment effect. Feng et al. [45] found that combining the heat and acid treatment could improve the power production to 1370 mW m^{-2}, which was 34% greater than the untreated control, 25% higher than using only the acid treatment and 7% higher than that using only the heat treatment.

3.2. Evaluation and measurement of electrode materials

It is very important to choose appropriate parameters and methods to evaluate and analyze the performance of electrode materials. The electrode potential at different current densities is considered to be an important parameter to evaluate the performance of electrode. The electrode potential can change the cell surface properties, increase the enzyme activity and shorten the doubling time of the bacteria [46,47]. According to the working principle of MFCs, the microbial activity in the anode is essential to liberating electrons from various organics, and the anode potential is one of the determining elements for the collection of energy from the microorganisms [48]. Meanwhile the cathode potential affects the redox reaction of the electron acceptor and electrons. Commonly, the measurements of electrode potential are conducted at different current densities in a three-chamber electrochemical cell containing a working electrode, a counter electrode and a reference electrode. Aelterman et al. [49] indicated that the anode potential could regulate both the activity and the growth of bacteria to sustain enhanced current and power generation. Liang et al. [50] studied the effects of cathode potentials on a biocatalyst by operating the biocathode at different selected cathode potentials. They indicated that an optimal cathode potential of 242 mV enhanced the performance of a biocathode that used oxygen as the electron acceptor.

In addition, many other electrochemical and material analysis methods have been adopted to evaluate the electrode characteristics of MFCs.

3.2.1. Cyclic voltammetry (CV)

As a standard tool in electrochemistry, CV has been widely used in MFCs to investigate the mechanisms of electrode reactions and to evaluate the performance of electrode materials and catalysts [46]. CV experiments generally require a three-electrode configuration to obtain accurate results. The anode or cathode is used as the working electrode; the other electrode is designated as a counter electrode, while the third lead is attached to a reference electrode (e.g., Ag/AgCl) [51].

Many studies on the electrode materials of MFCs have chosen CV to analyze performance. Adachi et al. [52] evaluated the performance of the modified anode by CV. The performance of the modified anode was dependent on the bioavailability and redox potential of the mediator (Med). They used a graphite felt plate as the base materials, and prepared three anodes that were modified by 1,5-pentanedioic acid (PA), 9,10-anthraquinone-2,6-disulfonyl (AQDS), and polyethyleneimine (PEI). It was observed directly through CV that different modified materials had different oxidation/reduction peaks, which could explain the effect of modification.

3.2.2. Electrochemical impedance spectroscopy (EIS)

EIS is a more advanced measurement to determine several electrochemical properties of the electrodes of MFCs, such as internal resistance and coating layers [53]. EIS measurement is a fairly simple procedure that is conducted using instruments such as a potentiostat. The potentiostat can be programmed to determine impedance spectra in a wide frequency range, such as from 100 kHz to 1 mHz. For MFC studies, 1 or 5 mHz should be sufficient as the lower frequency is limited in providing accurate information. Information about the electrochemical reactions that occur on electrodes, and the surface and material properties of electrodes can be obtained the EIS measurement of an individual electrode [54]. Manohar et al. [55] used EIS to evaluate the electrochemical behavior of the anode and the cathode of a mediator-less MFC. They considered the internal resistance can be determined through data of the impedance spectra at different cell voltages.

3.2.3. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a common technique for material analysis. It can observe and study the morphology of many materials, and recently it has been used in MFCs research [56]. Scott et al. [43] used the SEM photographs of modified carbon anode materials to directly reflect characteristics such as roughness and porosity. Yu et al. [57] applied SEM to analyze the morphology and composition of the catalysts and proved that the application of FePc on Ketjenblack (KJB) produced a highly irregular surface with an open structure.

In addition, during the analysis of the electrode materials, XPS and BET are also applied, which can help to understand the surface and element composition and thus assist in exploring possible mechanisms for the performance [44].

As is well known, most parameters, for example, power density, cell voltage, and Coulombic efficiency, have been used to measure the whole MFC reactor. Therefore, similar parameters, such as power density, could be used to indirectly reflect the performance of electrode materials when the studies of different electrodes are conducted under otherwise identical conditions. Yuan et al. [58] compared the power density versus the current density curves with various cathodes and found that the power density of the PPy cathode was higher than that of the carbon black cathode alone, suggesting that PPy contributed to the power enhancement.

4. Effect of electrode materials on wastewater treatment

The most promising application of MFCs is their use in wastewater treatment technology. Compared with other biological wastewater treatment processes, MFCs have many advantages, such as high theoretical energy conversion rate, less sludge and no gas processing. Therefore, recent developments have brought this technology from the early stage of simulated wastewater treatment to real wastewater disposal.

Table 5 lists some electrodes in MFCs that have been used to treat real wastewater. As shown in the table, the common electrode materials that are applied in the actual wastewater treatment are currently carbon cloth and carbon paper, while the cathode catalyst that is used nearly always contains Pt (0.35–1.12 mg cm^{-2}). Different wastewaters have different physical and chemical characteristics, so the treatment performances of MFCs differ considerably, in which the COD removals vary from 30% to 98%, but mostly reach levels >50%, although the output power of MFCs for different wastewaters alter greatly from 25 to approximately 3000 mW m^{-2}.

Domestic wastewater is an important source of sewage, and might be the most common substrates for MFCs. Though the quality of this wastewater is very similar and relatively simple, the performance of MFCs varied considerably due to different MFC constructions and electrode materials. For example, the COD removal varied from 25% to 80%, while the power density ranged from 25 to 400 mW m^{-2}. Even for similar wastewater qualities and MFC configurations, the performance still differed significantly because of different electrode materials. As was shown in previous stud-

Table 5
Examples of real wastewater that has been treated by MFCs with different electrodes.

Anode materials/area (cm^2)	Cathode materials/area (cm^2)	Wastewater	Configuration	Volume (mL)	P_{max} (mW m^{-2})	COD removal (%)	Reference
Carbon paper/100	Carbon cloth(0.5 mg cm^{-2},Pt)/100	Domestic sewage	Flat MFC	22	43	79	[8]
Carbon paper/22.5	Carbon cloth (0.5 mg cm^{-2}, Pt)/22.5	Food processing wastewater	DCMFC	125	81	95	[78]
Carbon paper/7	Carbon paper (0.35 mg cm^{-2},Pt)/7	Swine wastewater	SCMFC	250	261	92	[53]
Carbon paper/25	Carbon paper (1.12mgcm^{-2},Pt)/17	Starch wastewater	SCMFC	–	239.4	98	[79]
Carbon cloth/7 Carbon cloth/7	Carbon cloth (0.5 mg cm^{-2}, Pt)/7	Primary clarifier effluent	SCMFC	–	464	40-50	[58]
	Carbon cloth (0.35 mg cm^{-2}, Pt)/7	Brewery wastewater	SCMFC	–	205	87	[15]
Graphite rod	Carbon cloth (0.5 mg cm^{-2}, Pt)	Primary clarifier effluent	SCMFC	–	26	80	[6]
Graphite cylinder/20	Porous graphite bar/20	Domestic wastewater	Tubular MFC	–	25	~50	[80]
Graphite plates/25	Graphite plates/25	Distillery wastewater	SCMFC	500	124.35	72.84	[81]
Plain graphite electrode	Plain graphite electrode	Chemical wastewater	DCMFC	750	~125	35.4	[82]
Graphite granules + graphite rod	Woven graphite mat	Hospital wastewater	SCMFC	–	48*	–	[83]
Activated carbon + carbon cloth	Carbon cloth (0.5 mg cm^{-2}, Pt)	Fermented wastewater	SCMFC	250	2981	93	[84]
Carbon fiber/7	Stainless steel net (0.8 mg cm^{-2}, Pt)/7	Brewery wastewater	SCMFC	28	264	40	[59]
Carbon felt/10	Graphite paper/10	Electroplating wastewater	DCMFC	220	1600	99.5	[85]
Carbon fiber brush	Carbon fiber brush	Coking wastewater	DCMFC	18	51.2*	~100	[86]
Graphite fiber brush	Graphite fiber brush	Paper recycling wastewater	SCMFC	300	672	29	[87]

*W m^{-3}. SCMFC – single-chamber MFC; DCMFC – double-chamber MFC.

ies [6,59], the former exhibited a higher COD removal (80%) but a lower power density (26 mW m^{-2}) on the MFC with an anode of graphite rod; in contrast, the MFC with a carbon cloth as the anode demonstrated a much lower COD removal (40–50%) but had a higher power density (464 mW m^{-2}).

In addition, MFCs are also suitable for the treatment of some industrial wastewater. Generally, the COD of these wastewaters are higher than those of domestic wastewaters, and they varied greatly in different industries. It was observed that for wastewater from some food-related industries (e.g., food processing, brewery, starch and fermentation), the COD removal (>90%) was much higher than those in domestic wastewater (<80%). Also, as was the case in domestic wastewater, the importance of electrode materials in the MFCs, even given similar wastewater and MFC configurations, was shown. For example, for brewery wastewater, Wang et al. [15] and Feng et al. [60] used different electrode materials, showing that the power density of carbon cloth is slightly lower than that of carbon fiber, but its COD removal was much higher.

Also as is listed in Table 5, most of the electrode areas in the present studies for wastewater treatment ranged from several to 100 cm^2, which leads to the treatment volume that is far below that needed for practical application (limited to less than a 750 mL scale). Due to the microbiological, technological and economic challenges that need to be resolved in the scaling up of MFCs, at present most of the works are restricted to a lab scale; the pilot or full-scale implementation of MFCs is rather rare. It was reported that the Advanced Water Management Centre in the University of Queensland had constructed a pilot-scale microbial fuel cell for brewery wastewater treatment that had a volume of approximately 1 m^3 and consisted of 12 modules, using carbon fibres as both anodes and cathodes [61].

Alhough MFCs have the advantage of low operation cost and recovery energy (e.g., electricity or hydrogen) to improve their economic feasibility for wastewater treatment, they are not so cost-effective accounting for the high capital costs. It was reported that, based on the materials currently used in the laboratory, the capital costs of a full-scale MFC (8€ (kg COD)$^{-1}$) would be orders of magnitude higher than those of conventional wastewater treatment systems (0.01–0.1€ (kg COD)$^{-1}$) [62]. It should be noted that the contribution of the anode and cathode to the total capital cost was 9.4% and 47%, respectively. Therefore, it will be a great challenge to invent inexpensive substitute electrode materials to reduce the cost of future MFCs to implementable levels. Moreover, the lifetimes of electrode materials are currently seldom been reported or evaluated in wastewater treatment, an aspect that is urgently needed by life cycle assessment for future large-scale applications.

5. Problems and prospects

In the last two decades, many efforts have been made in the development and modification of electrode materials to promote the performance of MFCs. However, the present MFCs technology is still far from satisfactory for industrial application. In summary, there are still many problems to be resolved in the area of electrode materials, which might also be the topic of research trends in the future.

(1) The cost of electrode materials is still a key factor limiting their practical application. Though relatively high output power can be produced using carbon cloth and carbon paper, their prices are nevertheless expensive. Additionally, due to the limitations posed the traditional two-dimensional electrode, the promotion of MFCs performance will inevitably increase electrode and reactor sizes, which is bound to increase investment costs. Thus three-dimensional MFCs might have more potential future although some of the present works have demonstrated some advantages.

In addition, using the common catalyst Pt on the cathode increases the cost of MFCs. In recent years, the dawn of the biocathode may inspire one future research direction. A cathode with the presence of microorganisms can increase the spread of oxygen to the cathode and improve the rate of oxygen reduction [63]. Additionally, it can produce valuable new products or remove some compounds by the metabolism of microorganisms in the cathode. Therefore, many characteristics, such as simple construction, low operating costs, and not requiring a metal catalyst or an artificial electron mediator, result in biocathodes improving MFCs [64].

(2) Although some attempts at electrode modification have considerably improved the performance of MFCs, the mechanism is not yet very clear at present. Can we find a more cost-effective electrode fabrication method? As a potential wastewater treatment technology, the long-term stability of electrode materials is also a very important issue. However, most of the present studies have paid much more attention to the output power, not fully discussing the stability of the electrode materials, which would not provide valuable guideline for their long-term service in industrial application.

(3) Due to the complexity of the actual wastewater, one cannot hope that MFCs will solve all pollution problems. Therefore, the integration/combination of MFCs with other existing wastewater treatment processes (e.g., UASB) seems to be more feasible and calls for future study. For example, Zhang et al. successfully used a UASB–MFC–BAF system to dispose of complex molasses wastewater and achieved a power density of 1410.2 mW m^{-2} [65].

6. Conclusions

This review summarizes various electrode materials that have been used in MFCs for improved power output as well as their effects on many kinds of wastewater treatment. It demonstrated that different electrodes exhibited different behaviors and electrode modification proved to be a good alternative for enhancing the performance of MFCs. From the perspective of current development, the exploration of electrode materials will be more important and attractive as a reasonable price and excellent performance will greatly expand the application of MFCs. For wastewater treatment, the process integration/combination of MFCs with the present wastewater treatment technologies seems to be more promising, cost-effective and feasible.

Acknowledgements

This work was supported by NCET (08-0296), the Natural Science Foundation of Tianjin (no. 09JCYBJC08000), the National Water Project (nos. 2008ZX07526-002 and 2008ZX07314-001), and SRF for ROCS, SEM (2009-1001).

References

[1] B.E. Logan, Water Sci. Technol. 52 (2005) 31–37.
[2] Z. Du, H. Li, T. Gu, Biotechnol. Adv. 25 (2007) 464–482.
[3] B.E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Environ. Sci. Technol. 40 (2006) 5181–5192.
[4] H. Liu, S.A. Cheng, L.P. Huang, B.E. Logan, J. Power Sources 179 (2008) 274–279.
[5] K. Watanabe, J. Biosci. Bioeng. 6 (2008) 528–536.
[6] H. Liu, R. Ramnayanan, B.E. Logan, Environ. Sci. Technol. 38 (2004) 2281–2285.
[7] S.J. You, Q.L. Zhao, J.N. Zhang, J.Q. Jiang, C.L. Wan, M.A. Du, S.Q. Zhao, J. Power Sources 173 (2007) 172–177.
[8] B. Min, B.E. Logan, Environ. Sci. Technol. 38 (2004) 5809–5814.
[9] Z. He, S.D. Minteer, L.T. Angenent, Environ. Sci. Technol. 39 (2005) 5262–5267.
[10] H. Liu, S.A. Cheng, B.E. Logan, Environ. Sci. Technol. 39 (2005) 5488–5493.
[11] K. Swades, H. Chaud, D.R. Lovley, Nat. Biotechnol. 21 (2003) 1229–1232.

[12] Y. Ahn, B.E. Logan, Bioresour. Technol. 101 (2010) 469–475.
[13] B.E. Logan, S.A. Cheng, V. Watson, G. Estadt, Environ. Sci. Technol. 41 (2007) 3341–3346.
[14] J.R. Kim, S.H. Jung, J.M. Regan, B.E. Logan, Bioresour. Technol. 98 (2007) 2568–2577.
[15] X. Wang, Y.J. Feng, H. Lee, Water Sci. Technol. 57 (2008) 1117–1121.
[16] X. Wang, S.A. Cheng, Y.J. Feng, M.D. Merrill, T. Saito, B.E. Logan, Environ. Sci. Technol. 43 (2009) 6870–6874.
[17] P. Liang, M.Z. Fan, X.X. Cao, X. Huang, Z.H. Huang, C. Wang, Environ. Sci. 29 (2008) 512–517 (in Chinese).
[18] Y. Qiao, C.M. Li, S.J. Bao, Q.L. Bao, J. Power Sources 170 (2007) 79–84.
[19] T.A. Sharma, L.M. Reddy, T.S. Chandra, S. Ramaprabhu, Int. J. Hydrogen Energy 33 (2008) 6749–6754.
[20] Y.J. Zou, C.L. Xiang, L.L. Yang, L.X. Sun, F. Xu, Z. Cao, In. J. Hydrogen Energy 33 (2008) 4856–4862.
[21] H.Y. Tsai, C.C. Wu, C.Y. Lee, E.P. Shih, J. Power Sources 194 (2009) 199–205.
[22] K. Donaldson, R. Aitken, L. Tran, V. Stone, R. Duffin, G. Forrest, A. Alexander, Toxicol. Sci. 92 (2006) 5–22.
[23] V.K.K. Upadhyayula, V. Gadhamshetty, Biotechnol. Adv. 28 (2010) 802–816.
[24] A.M.K. Esawi, M.M. Farag, Mater. Des. 28 (2007) 2394–2401.
[25] L.M. Sherman, Plast. Technol. (2007) 1–7.
[26] V.N. Popov, Mater. Sci. Eng. R 43 (2004) 61–102.
[27] E.T. Thostenson, Z.T. Ren, T.W. Chou, Compos. Sci. Technol. 61 (2001) 1899–1912.
[28] H.J. Dai, Surf. Sci. 500 (2002) 218–241.
[29] C. Dumas, A. Mollica, D. Feron, R. Basseguy, L. Etcheverry, A. Bergel, Electrochim. Acta 53 (2007) 468–473.
[30] H. Richter, K.M. Carthy, K.P. Nevin, J.P. Johnson, V.M. Rotello, D.R. Lovley, Langmuir 24 (2008) 4376–4379.
[31] A.T. Heijne, H.V.M. Hamelers, M. Saakes, C.J.N. Buisman, Electrochim. Acta 53 (2008) 5697–5703.
[32] H. Moon, I.S. Chang, B.H. Kim, Bioresour. Technol. 97 (2006) 621–627.
[33] S.A. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 364–369.
[34] J.M. Morris, S. Jin, J.Q. Wang, C.Z. Zhu, M.A. Urynowicz, Electrochem. Commun. 9 (2007) 1730–1734.
[35] P. Aelterman, K. Rabaey, H.T. Pham, N. Boon, W. Verstraete, Environ. Sci. Technol. 40 (2006) 3388–3394.
[36] D.Q. Jiang, B.K. Li, Biochem. Eng. J. 47 (2009) 31–37.
[37] P. Aelterman, M. Versichele, M. Marzorati, N. Boon, W. Verstraete, Bioresour. Technol. 99 (2008) 8895–8902.
[38] S.A. Cheng, B.E. Logan, Electrochem. Commun. 9 (2007) 492–496.
[39] D.H. Park, J.G. Zeikus, Biotechnol. Bioeng. 81 (2003) 348–355.
[40] J.R. Kim, B. Min, B.E. Logan, Appl. Microbiol. Biotechnol. 68 (2005) 23–30.
[41] M. Rosenbaum, F. Zhao, M. Quaas, H. Wulff, U. Schrőder, F. Scholz, Appl. Catal. B: Environ. 74 (2007) 261–269.
[42] D.A. Lowy, L.M. Tender, J.G. Zeikus, D.H. Park, D.R. Lovley, Biosens. Bioelectron. 21 (2006) 2058–2063.
[43] K. Scott, G.A. Rimbu, K.P. Katuri, K.K. Prasad, I.M. Head, Process Saf. Environ. 85 (2007) 481–488.
[44] B. Erable, N. Duteanu, S.M.S. Kumar, Y.J. Feng, M.M. Ghangrekar, K. Scott, Electrochem. Commun. 11 (2009) 1547–1549.
[45] Y.J. Feng, Q. Yang, X. Wang, B.E. Logan, J. Power Sources 195 (2010) 1841–1844.
[46] K. Fricke, F. Harnisch, U. Schrőder, Energy Environ. Sci. 1 (2008) 144–147.
[47] J.P. Busalmen, S.R. De Sanchez, Appl. Environ. Microbiol. 71 (2005) 6235–6240.
[48] U. Schrőder, Phys. Chem. Chem. Phys. 9 (2007) 2619–2629.
[49] P. Aelterman, S. Freguia, J. Keller, W. Verstraete, K. Rabaey, Appl. Microbiol. Biotechnol. 78 (2008) 409–418.
[50] P. Liang, M.Z. Fan, X.X. Cao, X. Huang, J. Chem. Technol. Biotechnol. 84 (2009) 794–799.
[51] F. Zhao, R.C.T. Slade, J.R. Varcoe, Chem. Soc. Rev. 38 (2009) 1926–1939.
[52] M. Adachi, T. Shimomura, M. Komatsu, H. Yakuwa, A. Miya, Chem. Commun. (2008) 2055–2057.
[53] B. Min, J.R. Kim, S.E. Oh, J.M. Regan, B.E. Logan, Water Res. 39 (2005) 4961–4968.
[54] Z. He, F. Mansfeld, Energy Environ. Sci. 2 (2009) 215–219.
[55] A.K. Manohar, O. Bretschger, K.H. Nealson, F. Mansfeld, Bioelectrochemistry 72 (2008) 149–154.
[56] H.Q. Hu, Y.Z. Fan, H. Liu, Int. J. Hydrogen Energy 34 (2009) 8535–8542.
[57] E.H. Yu, S.A. Cheng, K. Scott, B.E. Logan, J. Power Sources 171 (2007) 275–281.
[58] Y. Yuan, S.G. Zhou, L. Zhuang, J. Power Sources 195 (2010) 3490–3493.
[59] S.A. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 2426–2432.
[60] Y.J. Feng, X. Wang, B.E. Logan, H. Lee, Appl. Microbiol. Biotechnol. 78 (2008) 873–880.
[61] http://www.microbialfuelcell.org/www/index.php/Applications/MFC-Pilot.html.
[62] R.A. Rozendal, H.V.M. Hamelers, K. Rabaey, J. Keller, C.J.N. Buisman, Trends Biotechnol. 26 (2008) 450–459.
[63] G.W. Chen, S.J. Choi, T.H. Lee, G.Y. Lee, ae-H. Cha, C.W. Kim, Appl. Microbiol. Biotechnol. 79 (2008) 379–388.
[64] Z. Bi, Y.Y. Hu, J. Sun, Acta Sci. Circumst. 29 (2009) 1635–1642 (in Chinese).
[65] B.G. Zhang, H.Z. Zhao, S.G. Zhou, C.H. Shi, C. Wang, J.R. Ni, Bioresour. Technol. 100 (2009) 5687–5693.
[66] B.E. Logan, Microbial Fuel Cells, John Wiley and Sons, Inc., Hoboken, New Jersey, 2008, p. 63.
[67] http://www.incukms.org.tw/web/g/G01_Detail.aspx?sid=63.
[68] S. Ishii, K. Watanabe, S. Yabuki, B.E. Logan, Y. Sekiguchi, Appl. Environ. Microbiol. 74 (2008) 7348–7355.
[69] H.J. Kim, H.S. Park, M.S. Hyun, I.S. Chang, M. Kim, B.H. Kim, Enzyme Microbial Technol. 30 (2002) 145–152.
[70] P. Liang, M.Z. Fan, X.X. Cao, X. Huang, Y.M. Peng, S. Wang, Q.M. Gong, J. Liang, Environ. Sci. 29 (2008) 2356–2360 (in Chinese).
[71] F. Zhao, F. Harnisch, U. Schrőder, F. Scholz, P. Bogdanoff, I. Herrmann, Electrochem. Commun. 7 (2005) 1405–1410.
[72] Y. Li, A.H. Lu, H.R. Ding, S. Jin, Y.H. Yan, C.Q. Wang, C.P. Zen, X. Wang, Electrochem. Commun. 11 (2009) 1496–1499.
[73] J.Q. Wang, C. Li, Q. Tan, Technol. Water Treat. 35 (2009) 84–86 (in Chinese).
[74] L.X. Zhang, C.S. Liu, L. Zhuang, W.S. Li, S.G. Zhou, J.T. Zhang, Biosens. Bioelectron. 24 (2009) 2825–2829.
[75] X. Li, B.X. Hu, S. Suib, Y. Lei, B.K. Li, J. Power Sources 195 (2010) 2586–2591.
[76] I. Roche, K. Katuri, K. Scott, J. Appl. Electrochem. 40 (2010) 13–21.
[77] L. Deng, M. Zhou, C. Liu, L. Liu, C.Y. Liu, S.J. Dong, Talanta 81 (2010) 444–448.
[78] S.E. Oh, B.E. Logan, Water Res. 39 (2005) 4673–4682.
[79] N. Lu, S.G. Zhou, L. Zhuang, J.R. Ni, Biochem. Eng. J. 43 (2009) 246–251.
[80] M.A. Rodrigo, P. Cañizares, J. Lobato, R. Paz, C. Sáez, J.J. Linares, J. Power Sources 169 (2007) 198–204.
[81] G. Mohanakrishna, S. Venkata Mohan, P.N. Sarma, J. Hazard. Mater. 177 (2010) 487–494.
[82] S.V. Mohan, G. Mohanakrishna, B.P. Reddy, R. Saravanan, P.N. Sarma, Biochem. Eng. J. 39 (2008) 121–130.
[83] K. Rabaey, P. Clauwaert, P. Aelterman, W. Verstraete, Environ. Sci. Technol. 39 (2005) 8077–8082.
[84] J.Y. Nam, H.W. Kim, K.H. Lim, H.S. Shin, Bioresour. Technol. 101 (2010) S33–S37.
[85] Z.J. Li, X.W. Zhang, L.C. Lei, Process Biochem. 43 (2008) 1352–1358.
[86] Y. Luo, R.D. Zhang, G.L. Liu, J. Li, M.C. Li, C.P. Zhang, J. Hazard. Mater. 176 (2010) 759–764.
[87] L.P. Huang, B.E. Logan, Appl. Microbiol. Biotechnol. 80 (2008) 349–355.