Recent Advances in Sediment Microbial Fuel Cells

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Abstract: Sediment microbial fuel cell is a kind of microbial fuel cell with anode and cathode respectively placed in sediment and water, which can be used in the fields of power supply of low-power equipment and in-situ remediation of river and lake sediments. This paper introduced the related research, and summarized the principle, influencing factors, microbial community, and application.

1. Introduction

The problem of fossil energy depletion and environment pollution is serious nowadays. Seeking new clean energy and efficient pollution control methods has become the focus of environmental researchers. As a novel technology that could both output energy and degrade pollutant, microbial fuel cell (MFC) converts chemical energy to electricity directly by a particular type of microorganism. Due to the characteristic of energy recovery, MFCs are considered to be a promising new technology that attract attentions of scholars in many fields. The microorganisms that close to anode oxidate the organic matter and transfer the electrons to anode. Electrons transfer to the cathode through an external circuit, and eventually react with oxygen and protons to form water. In this process the organic pollutants are degraded when the chemical energy is converted into electrical energy. Sediment microbial fuel cell (SMFC) is a special MFC with the anode buried in sediment and the cathode placed in water. It can be used for in-situ remediation of sediment with the relatively low cost and simple equipment maintenance. It was the first time that Reimers et al. proposed to harvest energy from the marine sediment with SMFCs in 2001. The recent researches are focused on optimizing the electricity generation performance of SMFC, exploring the organic matter degradation mechanisms and the feasibility analysis of the practical engineering applications.

2. Principle of Sediment Microbial Fuel Cell

SMFC consist of the anode buried in the anoxic sediment and the cathode placed in the aerobic water. The electro-microorganisms in the sediment which utilize oxidizable carbon compounds and other components transfer electrons to the anode. Dissolved oxygen in water and protons diffuse from sediment combine with electrons that transfer through the external circuit to form water and generate electricity. The fundamental cause of electricity generation is the redox potential difference between the water which contains oxidant and the sediment which contains reductant. The redox potential difference is closely related to the microbial activity in sediment. With the increase of the depth of the sediment, the dominant microbial community is different that from aerobic microorganisms to anoxic...
even anaerobic microorganisms. Microorganisms that exist in the lower layer of sediment utilize the organic matter and produce the reductant at the same time which results in the redox potential difference between anode and cathode. The electrons transfer from low potential to high potential, in other words, SMFCs generate current because of the redox potential difference.

3. Factors that Influence SMFC

As a new technology, sediment microbial fuel cell is affected by more factors in terms of operation and management compared to conventional batteries and common biological treatment processes. Therefore scholars in related fields have done a lot of researches mainly focus on electrode materials and design, operational conditions, sediment properties and microorganisms.

3.1. Electrode Materials and Design

3.1.1. Electrode Materials

Anode is important in terms of microbial attachment and electron transfer. Therefore, the anode materials should possess the characters of high specific surface area, good conductivity, corrosion resistance, biocompatibility and chemical stability. Graphite, carbon paper, carbon cloth, carbon sponge and other carbon based materials are often used as anodes materials because of the good conductivity and biocompatibility. However various carbon materials differ in shape, porosity, and so on, that results in the difference in electricity generation performance. The power output of SMFC using carbon sponge as the anode is higher than carbon cloth, carbon fiber and reticulated vitreous carbon. The comparison of granular active carbon (GAC) with carbon fiber brush (CB) and activated carbon nanofibers (ACNF) demonstrates that CB and ACNF outperform GAC because of higher interfacial bioavailable surface area, interconnectivity and conductivity [1].

3.1.2. Electrode Area and Spacing Distance

Electrode is one of the important factors that determine the rate of redox reactions and energy output. The rate of reaction between electrons and oxidant on the cathode increases with the area of cathode. Nevertheless, oversize electrode may impact the operation performance. Although the power generation scales almost linearly with anode size up to about 1~2 m², anodes larger than this can significantly decrease the power density result from the majority of losses along the anode surface that occur closest to the electronics.

The influence of electrode spacing distance on the SMFC is mainly reflected in the internal resistance. The ohmic resistance increases with more sediment and water and the polarization resistance of cathode increases with more soil while that of anode increases with more water. Thus, the power density decreases with the electrode spacing distance which depends on the water depth due to the reduction in internal resistance[2]. On the other side, despite the increase in the internal resistance the maximum power and current of the SMFC increased with the anode-embedding depth as a result of the more negative anode open circuit potential. Therefore, the trade-off point between the internal resistance and the MFC power output is important.

3.1.3. Electrode Modification and Improvement

In order to improve the electricity generation performance, a large number of researches related to anode and cathode were accomplished. Application of the porous electrodes in SMFC showed a superior performance in terms of generating current compared with non-porous electrodes because of increasing the specific surface area. On the other hand, pretreatment, modification and optimization design of the electrode type would enhance the electrochemical activity.

Different pretreatment would improve the performance of anode more or less. The performance of the SMFC with graphite anode coated with manganese oxide/multiwall carbon nanotubes (MWCNTs) composites is improved benefiting from the surface wettability, three-dimensional electronic conductivity of MWCNTs and Mn-related bacteria enrichment. Modification is a sufficient way to
improve the electron transfer and the mass transport efficiencies.
SMFC power output is restricted to the slow oxygen reduction reaction on the cathode that could be mitigated by reducing the activation energy with catalysts. The cathodes modified with multi-walled carbon nanotube improve the maximum power density to 1.6~3.2 times that of unmodified cathodes because of the increased electrochemical activity and oxygen reduction rate significantly[3]. Activated carbon cathode modified with polytetrafluoroethylene is more effective as well, so that the electricity generation performance is significantly improved[1].

Optimizing the design of the electrode type is another method to improve the performance of SMFC. Connecting electrode assemblies in series shows sustainable power production with decrement in ohmic and activation losses. SMFC with multiple-electrodes configuration would generate significantly more power[1].

3.2. Operational Conditions

3.2.1. Temperature
Microorganisms, the key of the power output are crucial in the microbial fuel cells. Temperature significantly affects the metabolic rate of the microorganism and power output performance. Although there is no significant effect on power output when sediment temperature range from 20°C to 35°C, system performance is negatively affected when the temperature is as low as 10°C. The current output of SMFC in winter when sediment temperature ranged from 10 to 13°C decreases significantly, by more than one-half, compared to that in spring and summer. As a result, the appropriate environmental temperature is necessary to ensure the stability of SMFC and hence causes attentions in the engineering application[2].

3.2.2. Water Properties
O2 is the most common terminal electron acceptor in the SMFCs. Therefore, the amount of current output is closely related to the concentration of dissolved oxygen(DO) at the cathode. There is a critical concentration that the electricity generation is not affected any more when DO is above it. The critical concentration influenced with many factors differs in various SMFC. Aeration, stir or utilizing floating cathode promote the oxygen reduction reaction near cathode. The in situ treatment of aquaculture pond water by SMFCs operated with aeration shows higher pollutant removal efficiency and power density than that without aeration.

The actual water pH in SMFC increases because of cathodic reactions consuming protons. Higher pH is conducive to electricity production and the enrichment of electrogenic bacteria[4] because that more electro-chemically active microbe is achieved in alkaline environment.

3.3. Sediment Properties

3.3.1. Sediment Type
The difference in the organic substance and microbial community among various sediments is great. As a result, the electricity output of SMFCs is different significantly as well. Compared to marine sediment, freshwater sediment is lack of salt, so that the conductivity is low. Therefore, the maximum
current density of freshwater sediment MFC is low result from the high internal resistance. In addition, the power output of tidal river sludge-MFC is between that of freshwater SMFC and that of marine SMFC.

3.3.2. Sediment Pretreatment

Sediment pretreatment could improve the performance of SMFC in different ways. The power output is limited partly by the low organic content of the sediment. Addition of carbon source is a method to solve this problem effectively. The concentration of organic matter is increased with addition of chitin, cellulose or biomass like leaves and wheat straw[5]. The appropriate supplement could decrease the internal resistance and enhance and lengthen power production. The added biomass could increase the cellulase activity and the contact opportunities between matrix, anode and microorganism, hence increasing the power production. However, the addition of excessive amount cellulose would cause accumulation of fatty acids due to microbial fermentation and decrease of pH, so that inhibits microbial activities and power output. In a word, the type and dosage of addition carbon source is important to improve the performance of SMFC.

The internal resistance could be decreased by adding the conductive substance to improve the electron transfer and power output. The appropriate addition of graphite flakes to the sediment shows higher electrogenic activity of SMFC. Pretreatment by mixed solution including soluble ferric citrate and colloidal iron oxyhydroxide, steadily improves SMFC performance with power outputs up to three folds higher than unmodified system because of lower anode potential and high-concentration ferrous iron as electron shuttle.

3.4. Microorganisms

3.4.1. Anode Microorganisms

All the energy-harvesting anodes are highly enriched in microbes in δ-Proteobacteria. Geobacteraceae accounts for the majority of δ-Proteobacterial microorganisms recovered from anodes (45-89%). Nearly all the Geobacteraceae in marine and salt-marsh sediments are most similar to Desulfuromonas species (83-89%). However, in freshwater sediments, all the Geobacteraceae are most closely related to Geobacter or Pelobacterpropionicus. G. psychrophilus and its related species preferentially grow on the anodes of rhizosphere SMFCs and generate electricity through syntrophic interactions with organisms that excrete electron donors[6]. Not only the sediment type, but also the depth of anode affect the anode organisms. The microbial biofilms on anode surfaces reveal changes in microbial community composition as a function of sediment depth and surrounding geochemistry.

3.4.2. Cathode Microorganisms

The biofilms formed in the water on the surface of cathodes could increase the current density of SMFC because of the efficient catalysis of the oxygen reduction, especially the phototrophic microbial biofilm that could promote oxygen generation at the same time. The utilization of photosynthetic process of the algae including microalgae and cyanobacteria at the cathode is an effective strategy to increase the oxygen availability to the cathode and the current output. Meanwhile, the algal concentration increases as a result of the synergetic interaction between algal culture and SMFC. In other words, CO₂ generated by bacterial activity is consumed by algal cultivation, and the O₂ produced from the algae is consumed by the SMFC cathode for current generation. The bacteria related to Acidiferro bacter thiooxydans and Marinobacter spp. that both belong to γ-Proteobacteria are enriched on the cathodes of plant-microbial fuel cell and microbial solar cell respectively[7].

4. Application of SMFC

As a microbial fuel cell, SMFC can produce considerable electrical energy that used as the energy source of low-power consuming device. On the other hand, SMFC is an alternative in situ bioremediation method due to the degradation of the organic pollutants during the power production. Currently, powering the low-power device and bioremediation is the main application of SMFC.
technology.

4.1. Power Supply
SMFC with less maintenance and long duration of the power generation could be used as the energy source of the low-power consuming device for environmental monitoring and oceanographic survey. The problem that the operation life of remote monitoring instrument is limited by the battery which is difficult to replace is solved partially with SMFC. The related scholars have conducted several researches on the supply of electricity for low-power devices and achieved high power density electricity by the storage of energy with capacitor.

4.2. Bioremediation
SMFC could not only generate power but also remove the organic pollutants without addition of oxidant compared to the traditional in situ bioremediation technologies[8]. Meanwhile, the organic matter in SMFC around the electrochemically-active anode becomes more humified, aromatic and polydispersed, and has a higher average molecular weight. In the freshwater sediment MFC, the removal efficiencies of phenanthrene and pyrene in the sediment is 20% higher than natural attenuation. The dibenzothiophene removal in the SMFC that aimed to maximize bioremediation of organic pollutants is enhanced by more than 3 folds compared to the natural degradation. The degradation of the total petroleum hydrocarbons is significantly improved in the SMFC while applying SMFC technology to contaminated sediments.

5. Outlook
SMFC achieves sustainable development by harvesting electricity from organic pollutants. Although SMFC has already removed contaminants and recovered energy successfully, more researches are required for the engineering application and further understanding of principle. (1) Electrode optimization: The anode materials with high specific surface area, chemical stability and conductivity and the cathode catalysts with high efficiency and low-cost are necessary for engineering application. And the research on bio-cathode is still insufficient currently. (2) Mass transfer of sediment: Only the organic matter near the anodes decreases obviously so that the slow mass transfer rate is a special problem of SMFC compared to other MFCs. (3) Temperature: Temperature is an important factor to affect microbial activity. The performance of SMFC is inhibited significantly at low temperature. Therefore, temperature must be considered in the SMFC especially during the engineering application when it is more difficult to control.

In addition, the SMFCs combined with plants in which electricity can be generated by microorganisms that use root exudates as fuel require further researches due to the good electricity generation performance and microbial activity. The integrated process of sediment fuel cell and electro-Fenton technology is proposed recently for first time and needs to explore further. The research on microorganisms in SMFC such as the functional genes and physiological characteristics is insufficient either.

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