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Electricity Generation by Biocathode Coupled Photoelectrochemical Cells

Yue Du,[a] Youpeng Qu, [*a, b] Xiangtong Zhou,[a] and Yujie Feng,[*a]

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Biocathode coupled photoelectrochemical cell (Bio-PEC) holds the potential of electricity recovery and pollutant removal with simultaneous utilization of both solar energy and bioenergy. Yet the performances are influenced by many factors. In this work, crucial parameters, including pollutant types, electrolyte concentration and gas atmosphere of photo-anode, are investigated to optimize the Bio-PEC operation in terms of electricity generation.

Energy crisis and environmental pollution are two hurdles to achieve sustainable development of human society in the 21st century. Solar energy and bioenergy are environmentally friendly, renewable and inexhaustible; the application of solar energy and bioenergy for energy conservation and pollutant remediation has attracted much attention recently. Photoelectrochemical cell (PEC) is attractive with double environmental benefits, namely, electricity generation and photocatalytic degradation of organic wastes with the utilization of solar energy.[1-3] The main components of a PEC consists of a photoanode, where electrons at conductive band and holes in valance band are produced with the excitation of photons, and a cathode where reductive reaction, usually oxygen reduction reaction (ORR) takes place with the assistance of catalysts. The common cathode catalysts, such as noble or transition metal nanoparticles, suffered from high cost and short service life due to loss, agglomeration and poisoning during long term operation.[4]

Biological cathodes (Biocathodes) are appealing alternatives to the metal catalysts and intensively studied in the field of microbial fuel cell (MFC).[17] An aerobic biocathode is the electrochemically active biofilm that accumulates to the cathode surface and facilitates the 4–electron ORR.[5-6] Bergel *et al.* tested a sea-water fuel cell with stainless steel biocathode, and observed that the maximum power density decreased from 270 to 2.8 mW/m^2 after the biofilm was removed from the cathode, indicating the effective catalysis of ORR by the marine biofilms.[18] The oxygen-reducing biocathode MFC operated with passive air transfer was reported to yield a maximum power density of 554 ± 0 mW/m^2, which was comparable to that obtained with a Platinum cathode (576 ± 16 mW/m^2).[19] Besides, the stains of biocathode can be selected from natural environment; the rapid growth and multiplication of biofilm endows the biocathode with the high efficiency and reproducibility; the pollutants in the wastewater can be converted or completely eliminated through microbial metabolism.[7-9]

The biocathode coupled PEC (Bio-PEC) is explored for the first time to integrate the advantages of fast and unselected photodegradation of organic pollutants and efficient, reproducible, and cost-efficient oxygen reduction of biocathode.[10] The electricity recovery and pollutant degradation of Bio-PECs is influenced by many factors. The optimization of operational parameters was crucial for the application of Bio-PECs. In this work, the influencing factors, such as substrates, the electrolyte concentrations, and air and nitrogen sparging of anode solution are well investigated for electricity generation. The information may provide valuable insights for the optimization of Bio-PECs.

TiO_2 nanotube arrays fabricated on titanium sheet by electrochemical anodization method was used as photoanode. The biocathode used in this work was firstly enriched in a MFC reactor as described in detail in supporting information (Fig. S1). The biocathode was then taken out of the MFC and installed into the PEC reactor to construct the Bio-PEC (Fig. S2).

Dual chambered Bio-PEC was made of plexiglass with a quartz window to allow the transmission of UV light. The photoanode chamber and cathode chamber were separated by cation exchange membrane (Qianqiu Co. Ltd., China). A 150W xenon lamp (GY-10A, Tuopu Co. Ltd., China) was used as light source. The cathode solution was aerated with a pump in all experiments. The cathode part of PEC was wrapped by aluminium foil to shield the UV-visible light. The external resistance was kept at 1000 Ω for all experiments except for power density and polarization measurement. The anolyte was stirred by magnetic bar in dark for 20 min to ensure adsorption-desorption equilibrium prior to irradiation and continuously stirred during the experiment.

The output voltages (V) of Bio-PECs were recorded with a data acquisition board every one minute. The polarization curves were measured by recording the current response to a linear potential decrease imposed to the PECs at a scanning rate 10 mV/s using electrochemical workstation (Metrohm Autolab 85061). Power density was calculated by normalizing the power ($P = IV$) by the surface area of anode. Electrons harvested through external circuit (Q) was determined by integrating the current over time ($Q = \int Idt$).

The working principal of Bio-PECs involves the electron production through photocatalytic process in the photoanode and

electron consumption facilitated with exoelectrogens in the biocathode. With xenon illumination, the electrons on the surface of TiO_2 electrodes are excited from valance band to conduction band, yielding positive holes in valance band and negative electrons in conduction band (Eq. 1).[12] The electrons travel to the cathode through external circuit and are harvested as energy; while the holes oxidize the organic substrates, either directly or via ·OH radicals formed by the reaction with OH^- and/or H_2O in the solution (Eq. 2). In the solution, the cation, such as Na^+, H^+, K^+, will diffuse from anode chamber to the cathode chamber through the cation exchange membrane to complete the electricity production. The electron generation and organic oxidation of photoanode are closely related with the separating efficiency of hole/electron pairs which is mainly determined by photocatalysts. Other operation parameters, such as illumination intensity, organic substrates, electrolyte concentration, and gas atmosphere also influence the performance of photoanode which will be discussed in the following sections.

$$TiO_2 + h\nu \rightarrow h_{vb}^+ + e^- \quad (1)$$

$$h_{vb}^+ + H_2O \rightarrow \cdot OH + H^+ \text{ or } h_{vb}^+ + OH^- \rightarrow \cdot OH \quad (2)$$

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O \quad (3)$$

$$e^- + O_2 \longrightarrow O_2^- \text{ or } 2e^- + O_2 + 2H^+ \longrightarrow H_2O_2 \quad (4)$$

The biocathode, usually called aerobic biocathode or nitrifying biocathode from the functionality point of view, was dominated with ammonia oxidizing bacteria and nitrite oxidizing bacteria.[11] The electrochemical active biofilm catalyzed the oxygen reduction reaction in the cathode (Eq. 3) and meanwhile converted the ammonia in the catholyte to nitrate through microbial metabolism. The catalytic activity of oxygen reduction is closely related to the microbial activity: with suitable culture condition, such as nutrients and oxygen, the metabolism and multiplication of bacteria is faster thus results in higher catalytic efficiency.

Table 1 Power generation of Bio-PEC using various kinds of artificial wastewater as substrates.

	V_{oc} (mV)	I_{sc} (A/m^2)	$P_{cathode}$ (mV)	P_{anode} (mV)	Power$_{max}$ (mW/m^2)	pH
Methyl orange	690	1.87	302	-388	218	6.9
Acetate	730	1.51	299	-428	473	7.3
Glucose	715	1.74	305	-408	203	6.8
Glutamic acid	642	1.07	301	-352	96	3.5
Urea	668	1.40	308	-359	222	6.2

Various kinds of artificial wastewater were used as anode substrates for electricity generation (Table 1). The open-circuit voltage (V_{oc}) and short-circuit current density (I_{sc}) varied when different organic compounds were used. As the cathode potentials in open circuit condition ($P_{cathode}$) altered in a small range, from 299 to 308 mV, the difference in voltage and power output was mainly determined by anode performance. The Bio-PEC produced highest V_{oc} (730 mV), I_{sc} (1.87 A/m^2) and maximum power density (Power$_{max}$) (473 mW/m^2) with artificial acetate wastewater as substrate, respectively. The substrates in anode solution functions as not only the pollutants to be removed by photocatalytic process, but also as sacrificial agent for holes that improved the separation of hole/electron pairs. The role is similar to the methanol that is used as sacrificial agent for holes during hydrogen production through photocatalytic water splitting.[13] The acetate has simple molecular structure, and can be easily destroyed;[14] moreover, acetate radicals formed by hydrolyzation of acetate are negative charged, and can easily reach the positive charged holes. These made the acetate yielded higher performance in Bio-PECs.

Bio-PEC produced lowest performance with V_{oc} of 642 mV, I_{sc} of 1.07 A/m^2, and $Power_{max}$ of 96 mW/m^2 when glutamic acid was used as substrate among the artificial wastewater, which was probably due to the acidity of glutamic acid solution (pH = 3.48). The protons may react with photogenerated electrons and resulted in lower current density.[15]

In the typical process of fuel cells, electrons transfer from anode to cathode through external circuit, while cation moves from anode to cathode through the solution. The low electrolyte concentration will result in large cation transition resistance, low power output, and pollutant degradation, thus certain actual wastewater with low electrical conductivity is not suitable for treatment by Bio-PEC.

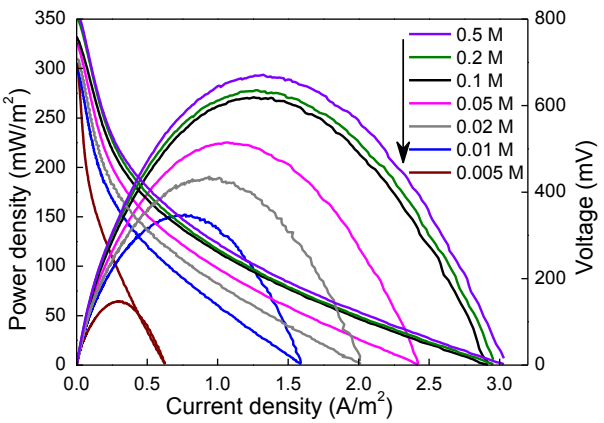

Fig. 1 Power generation and polarization curves of Bio-PECs with Na_2SO_4 concentrations in the anode solution 0.5, 0.2, 0.1, 0.05, 0.02, 0.01 and 0.005 mol/L, respectively.

To study the minimum conductivity requirement of wastewater, glucose (5 g/L) with different Na_2SO_4 concentrations (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 mol/L) was used as the substrates of photoanode (Fig. 1). The correlated electrical conductivities for each anode solution were 1.11, 2.10, 3.94, 8.80, 16.9, 29.8, and 57.8 mS/cm, respectively. The maximum power density and current density both improved with the increase of Na_2SO_4 concentration in anode electrolyte. The maximum power density increased by 2.5 times as the anolyte conductivity increased from 1.11 mS/cm (65 mW/m^2) to 8.8 mS/cm (225 mW/m^2). The increasement of maximum power densities from 270 to 293 mW/m^2 was negligible with the anolyte conductivities between 16.9 and 57.8 mS/cm. Although the higher conductivities of wastewater are more beneficial for power production, they are relatively low for most actual wastewater. For example, the electrical conductivities of pharmaceutical wastewater, brewery wastewater, and chicken steoprotegerin wastewater studied in our lab were 7.78, 3.28, and 44.50 mS/cm, respectively. Considering the electricity production and practical

situation in actual wastewater, the minimum requirement for solution conductivity should be around 10~15 mS/cm.

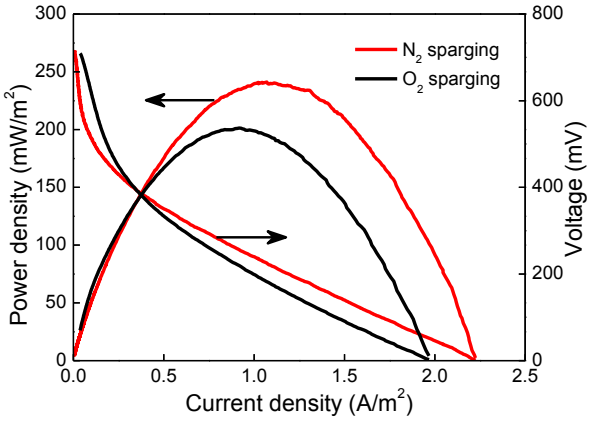

Fig. 2 Power generation and polarization curves of Bio-PEC with anode solution aerated with nitrogen and air for 30 min, respectively.

To evaluate the influence of gas atmosphere to the electricity generation characteristics, the anode solution (glucose 5 g/L and Na_2SO_4 0.05 mol/L) was firstly sparged with nitrogen and air for 30 min, respectively, before poured into reactor for measurement. When anode solution was aerated with air, the anode potential in open circuit condition was ca. –408 mV, the maximum current density was 1.76 A/m^2 and maximum power density was 203 mW/m^2 (Fig. 2). The nitrogen sparging obviously enhanced the performance of Bio-PEC with the anode potential in open circuit condition decreasing to –457 mV, the maximum current density increasing to 2.22 A/m^2 and the maximum power density 239 mW/m^2. In the air sparged solution, the oxygen may react with photogenerated electrons to form O_2^- or H_2O_2 (Eq. 4), which is also strong oxidant. The presence of oxygen in anode solution may contribute to the pollutant degradation. However, it also consumed electrons and resulted in lower power production. This was in good agreement with the previous study that investigated the effect of dissolved oxygen on photocatalytic reaction rate.[16]

Conclusions

In this work, influencing factors, such as substrates, electrolyte concentration and gas atmosphere of photo-anode are investigated in terms of electricity generation of Bio-PEC. As a representative of model compounds, the acetate produces the highest cell performance with short circuit current density of 1.87 A/m^2, open-circuit voltage of 730 mV, and maximum power density of 473 mW/m^2. The minimum electrical conductivity of wastewater for Bio-PEC system was 10~15 mS/cm, which avoided large ion transfer resistance in the solution. Nitrogen sparging of anode solution facilitated the electron generation compared with air sparging due to electron capture by oxygen.

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Notes and references

[a] *State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China. Fax/Tel: +86-451-8628 7017; Email: yujief@hit.edu.cn.*

[b] *School of Life Science and Technology, Harbin Institute of Technology, Harbin, 150080, China. Email: pp198259@hit.edu.cn.*

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