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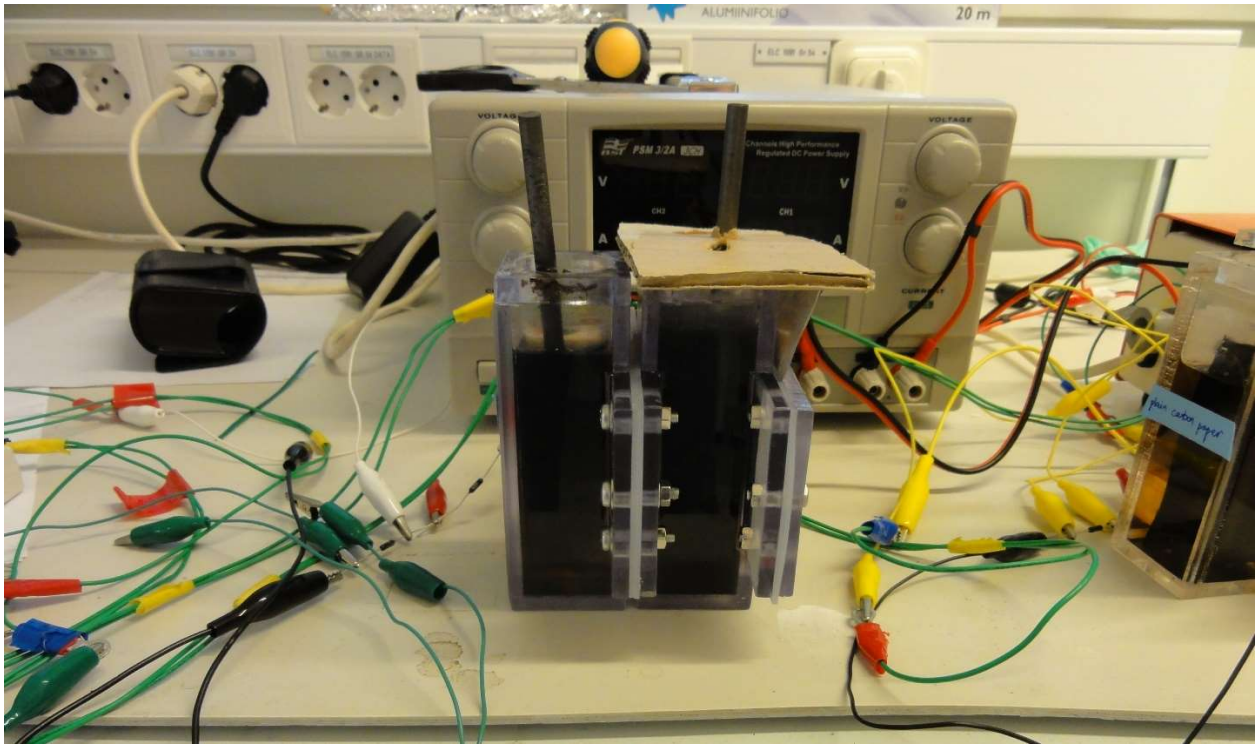

Investigation of cathodic O_2 reduction and development of a new bioelectrochemical BOD sensor

Master of Science Thesis in the Master's Programme Geo and Water Engineering

YU TIAN

DEPARTMENT OF ARCHITECTURE AND CIVIL ENGINEERING
DIVISION OF WATER ENVIRONMENT TECHNOLOGY

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Cover:
Microbial fuel cell with rod cathode

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Abstract

Microbial Fuel Cells (MFCs) have been investigated intensively during the last 20 years. Through MFCs, dissolved organic matters in wastewater can be removed and used as renewable energy for electricity production at the same time. The main impediment for increasing MFCs' efficiency is the high overpotential of the cathodic reduction. The catalyst and material of the electrode is essential to reduce the cathodic overpotential.

In this master thesis, the properties of three types of gas-diffusion cathodes were tested, 1) plain carbon paper without any catalyst coating; 2) carbon paper coated with carbon nanoparticles; and 3) carbon paper coated with platinum loaded activated carbon powder. Living bacteria in both aerobic and anaerobic culture were investigated as catalyst for the cathodes.

The results showed that the performance of the plain carbon gas-diffusion cathode is much worse than the cathode coated with nanoparticles. Pt showed the best cathodic catalysis while living bacteria gave no catalysis function. Anaerobic sludge even inhibited the cathode reaction. However, the performance of cathode coated with nanoparticles was stable in the presence of both kinds of sludge, which suggested that nanoparticles are suitable catalysts for single chamber MFCs.

In this project, we also investigated a single chamber MFC as a BOD sensor. BOD concentration was reflected as the total transferred charge. The response time was tested under two conditions, with 100ohm external resistance loaded and with an input voltage (1V) to accelerate the reaction. For the first condition, the response time was about 3.5 days, which is shorter than the conventional BOD measuring method, 5 to 7 days. And with an input voltage, response time was even shorter, only 1.25 days was used to obtain the BOD value.

Keywords

Microbial Fuel Cells (MFC); gas-diffusion electrode (GDE); cathodic oxygen reduction; bacteria catalysis; BOD sensor

Content

Glossary

Terms	Definition
BOD	biochemical oxygen demand
CV	cyclic voltammetry
DO	dissolved oxygen
E	cell voltage
E_{an}	theoretical anode potential
E_{cat}	theoretical cathode potential
$E^0_{cat/an}$	standard electromotive force
E_{emf}	maximum electromotive force
GDE	gas diffusion electrode
I	circuit
LSV	linear sweep voltammetry
MFC	microbial fuel cell
NHE	normal hydrogen electrode
OCV	open circuit voltage
$\sum OP_{cat/an}$	overpotential of cathode/anode
P	power
$R_{int/ext}$	internal/external resistance
R_Ω	ohmic resistance

Introduction

This introduction chapter contains the background to the studied subject and defines the specific goals as well as the limitations of the research.

1.1 Background

Dissolved organics in wastewater are required to be removed before discharging into the environment. In conventional treatment, these contaminants are mostly oxidized in the activated sludge process (see Figure 1-1), which requires large amounts of energy for aeration for the aerobic sludge process.

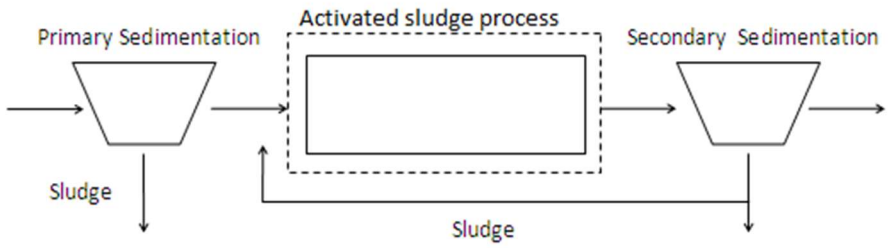

Figure 1-1 Schematic of the conventional treatment process in a common wastewater treatment plant.

Recently, organic matter in wastewater is increasingly considered as a renewable resource for the production of electricity, fuels and chemicals (Rozendal et al., 2008). However, in conventional wastewater treatment, the energy can only be recovered from the sludge using anaerobic digestion but not from the dissolved organic matter. As a result, an emerging technology for the treatment of aqueous organic pollutants, microbial fuel cells (MFCs) arise, which could be used for pollution control and energy recovery from the wastewater.

1.2 Principle of MFCs

MFC is a device that uses bacteria as catalyst to oxidize organic, converting chemical energy to electrical energy. An MFC contains an anode (negative terminal), a cathode (positive terminal). The oxidation takes place in the anode chamber. The produced electrons are released from the bacteria to the anode and then flow through an external circuit in the form of electric current to the cathode, where the electron acceptors are reduced.

Chemical oxidizers are commonly used as electron acceptors in MFC for their good performance of low overpotential, such as ferricyanide ($K_3[Fe(CN)_6]$) and Mn (IV). However, the catholyte needs to be regularly replaced or re-oxidized due to the insufficient regeneration by dissolved oxygen (Rabaey et al., 2005). In contrast, oxygen is more suitable as electron

acceptor because of its high oxidation potential, free of cost, availability, environmental friendly and sustainability. Since oxygen will hinder the electron generation, the system should be designed to keep oxygen away from the anode chamber (Logan, 2007). The schematic of an MFC can be seen in Figure 1-2.

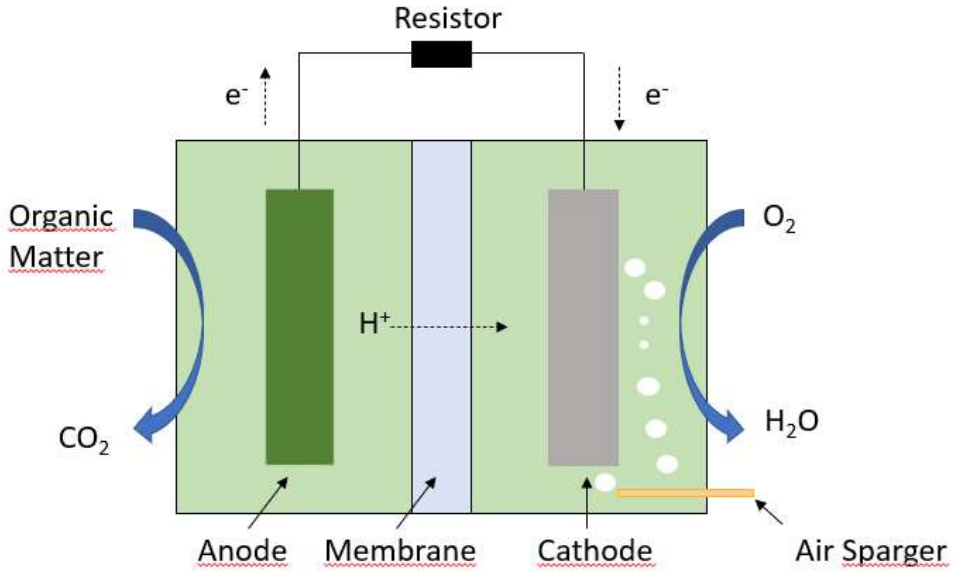

Figure 1-2 Illustration of the basic components of a microbial fuel cell, oxygen as the electron acceptor at the cathode (adapted from Logan, 2007). Anode and cathode chambers are separated by a membrane to prevent bacteria contact with oxygen. Degradable organic matter is oxidized in the anode chamber, giving electrons through an external circuit to the cathode where oxygen is reduced.

The chemical reactions that take place at the anode and cathode are shown below (acetate is the electron donor at the anode and oxygen is the electron acceptor at the cathode). Depending on the electrode material and the catalyst used, oxygen can be reduced directly to water or via hydrogen peroxide.

Anode: $CH_3COO^- + 4H_2O \longrightarrow 2HCO_3^- + 9H^+ + 8e^-$

Cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

$(O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O)$

Net reaction: $CH_3COO^- + 2O_2 \longrightarrow 2HCO_3^- + H^+$

Besides organic matter, MFCs could also be used to remove nitrogen in wastewater (Clauwaert et al., 2007). Therefore, in the future the active sludge process in conventional wastewater treatment might be replaced by microbial fuel cells to generate electricity from dissolved organics. During the last ten years, the power output of MFCs has continuously increased. Power output as high as 21 W/m^3 (cathode total volume) (Freguia et al., 2007) has been

produced. However, still much improvement is needed for practical application.

1.3 Aim

To make MFCs a useful method to recover power or clean wastewater efficiently, it is essential to solve the main impediment of high overpotential for the cathodic reduction (Freguia et al., 2010). Compared with non-sustainable electron acceptors, e.g., ferricyanide, oxygen is predicted to have a higher cathode potential, yet in practice the potentials achieved using oxygen are much lower than theoretical values (Logan, 2007). Therefore, catalysis is essential for the cathode reaction. The most commonly used catalyst is platinum. However, despite its efficiency, platinum is expensive and could lose its catalytic ability after prolonged exposure to various chemicals that are present in the wastewater. There is another possible catalyst, living bacteria. The possibility of bacteria to be cathode catalyst was shown by Rabaey et al. who used pure cultures of bacteria (Rabaey et al., 2008). Living bacteria are inexpensive and self-regenerating and could potentially improve the long-term operation of MFCs and reduce the cost. So far, not many studies have investigated if bacteria could catalyze oxygen reduction on gas-diffusion cathodes. Therefore, in this project, living bacteria in mixed culture will be investigated as catalysts for oxygen-reducing gas-diffusion cathodes.

The other aim of this project is to investigate MFCs as BOD sensors. Biochemical oxygen demand (BOD) is a common parameter that reflects the organic contents of wastewater. The conventional way of measuring BOD value always requires 5 to 7 days of incubating the samples with proper source of microbes, which is too time consuming when it is used as a real time control parameter. Since the oxidation of a substrate occurs with the removal of electrons (Logan, 2007), the amount of electrons transferred is directly proportional to the organic matter content in the wastewater. Therefore, an MFC could be another way of measuring BOD values. In this thesis project, a new type of MFC-based BOD senor is designed, and the possibility and accuracy of using MFCs as BOD sensor will be investigated and discussed.

Specific objects include:

- Investigate whether bacteria can improve the catalytic properties of (i) plain carbon fiber paper, and (ii) carbon fiber paper coated with carbon nanoparticles.
- Compare the performance of bacteria and platinum as cathode catalysts for GDEs.
- Analyze the effect of DO conditions on the cathode performances.
- Develop a new type of bioelectrochemical BOD sensor.
- Investigate the response time of the BOD sensor under varying operational conditions,

1.4 Limitation

Due to the complexity of the microbial catalytic mechanisms and the restrictions of the experiment facilities, some limitations have been defined in this thesis project and thus will not be taken into consideration:

- The mechanisms of electrochemical reactions, e.g., electron transfer pathways, etc.

- Microbial catalysis using specified group of bacteria or bacteria that is cultivated in certain nutrient solutions.
- The experiments in this project are all lab-based; scaling up issues are not considered.

Literature review

2.1 Voltage and Power Generation

2.1.1 Voltage generation

Voltage is the most visualized observation of an MFC, which is a function of circuit load R_{ext} and the current I. It can be calculated by the well-known equation $E=I*R_{ext}$, where E stands for the cell voltage. The highest voltage can be obtained under the infinite resistance, which is called the open circuit voltage, OCV. The cell voltage drops as the external resistance decreases.

In an MFC, cell voltage is hard to predict due to the complicated conditions of the solution and bacteria. However, the maximum potential in terms of the maximum electromotive force of each electrode follows the law of thermodynamics. Thus, the upper limit of cell voltage can be evaluated.

$$\mathrm{E}_{emf} = \mathrm{E}_{cat} - \mathrm{E}_{an} \qquad 2\text{-}1$$

Where E_{emf} is the maximum cell electromotive force, defined as the difference between the theoretical cathode potential (E_{cat}) and anode potential (E_{an}). The minus sign is a result of the definition of a reduction reaction in the anode although an oxidation reaction is occurring (Logan et al., 2006).

According to the Nernst Equation, the maximum cell electromotive force can be calculated as follows, under non-standard state conditions and at any time of the reaction.

$$\mathrm{E}_{emf} = \mathrm{E}^{0}_{cat/an} - \frac{\mathrm{RT}}{\mathrm{nF}}\ln(\Pi) \qquad 2\text{-}2$$

$\mathrm{E}^{0}_{cat/an}$: standard electromotive force of the terminals;

$\Pi = \frac{[\mathrm{products}]^{\mathrm{p}}}{[\mathrm{reactants}]^{\mathrm{r}}}$ where p and r are the stoichiometric coefficients of products and reactants;

R=8.31447 J/mol-K;
T: the absolute temperature (K);
n: the number of transferred electrons;
F=96485 C/mol.

All standard potentials (E^{0}) are calculated relative to the normal hydrogen electrode (NHE), which is defined to be $\mathrm{E}^{0}(H_2)=0$ under the standard conditions (298K, pH_2=1 bar, $[H^+]$=1 M). Note that equation 2-1 can only be used when the cathode and anode potential are calculated under the same pH value.

According to these equations, maximum cell voltage can be obtained for typical conditions in MFCs (See Table 2-1).

Table 2-1 Maximum cell electromotive forces for typical conditions in MFCs (Logan et al., 2006)

Electrode	Reaction	Conditions	$E_{cat/an}$ (V)	E_{emf} (V)
Anode	$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O$	HCO_3^- =5 mM, CH_3COO^-=5 mM, pH=7	-0.296	-
Cathode	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	pO_2 =0.2, pH =7	0.805	1.101
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	pO_2 =0.2, $[H_2O_2]$ =5 mM, pH =7	0.328	0.624
	$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	$[Mn^{2+}]$ =5 mM, pH =7	0.470	0.766
	$Fe(CN)_6^{3+} + e^- \rightarrow Fe(CN)_6^{4-}$	$[Fe(CN)_6^{3+}] = Fe(CN)_6^{4-}$	0.361	0.657

All potentials are shown with respect to NHE; cell voltages are calculated against acetate-oxidizing anode.

2.1.2 Factors that affect cell voltage

As seen in Table 2-1, the maximum theoretical cell voltage obtained from MFC using oxygen at the cathode is 1.1 V. However, the maximum predicted potential does not take into account internal losses and thus is always higher than the open circuit voltage (OCV). In practice, the maximum MFC voltage produced so far is 0.8 V (Liu et al., 2005) which is clearly lower than the predicted value of 1.1 V. This difference between the theoretical potential under equilibrium conditions and the measured potential is referred to as overpotential, which is the sum of electrode overpotentials and ohmic losses:

$$E_{cell} = E_{emf} - (\sum OP_{An} + |\sum OP_{Cat}| + IR_{\Omega}) \qquad 2\text{-}3$$

where $\sum OP_{An}$ and $|\sum OP_{Cat}|$ are the overpotentials of the anode and cathode respectively, and IR_{Ω} refers to all ohmic losses which are current-dependent and proportional to the system's ohmic resistance (R_{Ω}) (Logan, 2007). Electrode overpotentials are mostly current dependent and caused mainly by three basic losses: activation losses, bacterial metabolism losses and mass transport losses (Logan 2007).

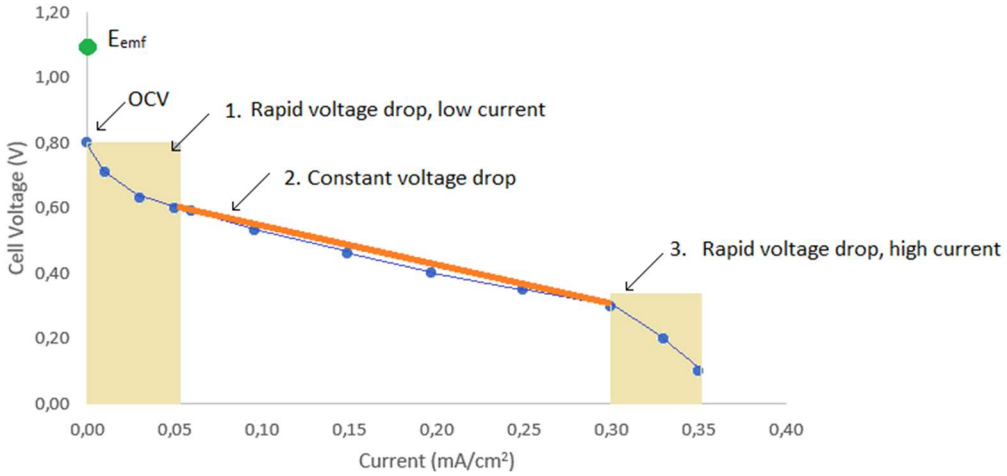

Figure 2-1 Characteristics of a polarization curve showing different regions where different types of losses are dominating (adapted from Logan, 2007).

***Ohmic losses*.** Ohmic losses include the resistance of the flow of electrons and ions through

the electrodes, interconnections and the electrolyte respectively (Logan et al., 2006). Ohmic losses can be cut by reducing the electrode spacing, selecting materials with low resistance, increasing solution conductivity within the bacterial tolerance range, and decreasing losses between each contact (Logan, 2007).They are the most importance losses to be reduced in optimizing an MFC system (Logan, 2007).

Activation losses. These losses arise from energy consumption in initiating the oxidation/reduction reactions and electrons transferring between electrode surfaces and compounds. Activation losses are most evident at low currents (the first region in Figure 2-1) (Logan, 2007). The losses can be reduced by improving electrode catalysis or optimizing the system operation conditions (Logan et al., 2006).

Bacterial metabolism losses. Bacterial metabolism losses are due to the energy consumptions from substrate oxidation for bacterial activities, *e.g.*, anabolic cell processes. These losses are inevitable (Logan 2007). The lower the difference between the substrate's redox potential and the anode potential, the lower voltage lost from bacterial metabolism (Logan et al., 2006). Therefore, the anode potential should be kept as low or as negative as possible (but still allow electron transport), so as to recover maximum power from a MFC.

Mass transport (concentration) losses. Mass transport (concentration) losses are voltage losses due to the lack of sufficient transportation of chemical species to or from the electrodes, which limits the rate of reactions. Different from activation losses, mass transport losses are mainly apparent at high currents as shown in the third region in Figure 2-1. Mass transfer limitation might cause the change in pH conditions in MFCs; an increase at the anode, and an elevated pH at the cathode (Kim et al., 2007). Sufficient buffer capacity should therefore be ensured in the system.

Over the medium range of current (between the low and the maximum generated current), measured MFC voltage always has a linear relationship with the produced current (Logan, 2007), which can be seen in Figure 2-1 in the region of constant voltage drop. Therefore, MFC performance can also be analyzed in terms of open circuit voltage (OCV) and internal losses (IR_{int}):

$$\mathrm{E}_{cell} = \mathrm{OCV}^{*} - \mathrm{IR}_{int} \qquad 2\text{-}4$$

where R_{int} is the sum of all internal resistances of the system and OCV^{*} is the y-intercept in Figure 2-1 (but not the true OCV due to the non-linear curve at low current).

A comparison between equation 2-3 and equation 2-4 indicates that the ohmic losses of the system (IR_{Ω}) together with the current dependent overpotentials of the electrodes are included in the internal losses (IR_{int}), while the electrode overpotentials under open circuit conditions are reflected in the value of OCV^{*} (Logan, 2007). Therefore, one should be aware that although the term of internal resistance (R_{int}) and ohmic resistance (R_{Ω}) are often used interchangeably, they are indeed different.

2.1.3 Power generation and Coulombic efficiency

As the final purpose of MFCs, power generation is often used to evaluate the overall performance of the system. Power is calculated as a function of the generated voltage and current,

$$\mathrm{P} = \mathrm{I}\mathrm{E}_{cell} \tag{2-5}$$

The voltage of the lab-scale MFC is normally measured over a fixed load (*e.g.*, the external resistor, R_{ext}) and the current is calculated using the equation, $\mathrm{I} = \frac{\mathrm{E}_{cell}}{\mathrm{R}_{ext}}$. Therefrom, power output can be derived from

$$\mathrm{P} = \frac{\mathrm{E}_{cell}^2}{\mathrm{R}_{ext}} \tag{2-6}$$

Considering the effect of the internal resistance, the total generated power is,

$$\mathrm{P}_{total} = \frac{\mathrm{E}_{cell}^2}{(\mathrm{R}_{int}+\mathrm{R}_{ext})} \tag{2-7}$$

Thus, the output power can be calculated as,

$$\mathrm{P} = \frac{\mathrm{E}_{cell}^2}{(\mathrm{R}_{int}+\mathrm{R}_{\mathrm{ext}})}\frac{\mathrm{R}_{ext}}{(\mathrm{R}_{int}+\mathrm{R}_{ext})} = \frac{\mathrm{E}_{cell}^2\mathrm{R}_{ext}}{(\mathrm{R}_{int}+\mathrm{R}_{\mathrm{ext}})^2} \tag{2-8}$$

As seen from equation 2-8, a maximum power output can be produced when $\mathrm{R}_{int} = \mathrm{R}_{\mathrm{ext}}$. It is therefore important to minimize the internal resistance to increase the power generation.

Besides the power generation, recovery of electrons which is referred to as coulombic efficiency (C_E) can also be used to analyze the performance of an MFC. It is defined as the ratio between the total transferred Coulombs and the maximum possible Coulombs if all removed substrate produces current. According to the definition, C_E can be calculated as

$$\mathrm{C}_E = \frac{\frac{\int_0^{\mathrm{t0}} Idt}{\mathrm{F}}}{\frac{\mathrm{V}_{an}\Delta\mathrm{c}}{\mathrm{M}}\mathrm{b}} = \frac{8\mathrm{I}}{\mathrm{Fq}\Delta\mathrm{COD}} \tag{2-9}$$

Where Δ c is the substrate concentration change over a time t0, V_{an} is the volume of liquid in the anode, b is the number of exchanged electrons per mole of oxygen, M is the molecular weight of oxygen, F is Faraday's constant and q is the flow rate for continuous flow.

2.2 Oxygen Reduction on Cathodes

On biologically catalyzed electrodes, extracellular electron transfer between bacteria and electrodes is achieved by means of exogenous electron mediators or by so-called nanowires produced by the bacteria, in which case the MFC is classified as a "mediator-less" MFC even

though the electron transfer mechanism may not be known yet (Logan et al., 2006). In an air cathode, oxygen is used as electron acceptor and oxidized to water on the cathode surface.

In the air cathode, oxygen is supplied either by air sparging or directly from the air. The first way of supplying oxygen is energy intensive and also requires enough space for an air sparger. As a result, the better option is to use a gas diffusion electrode (GDE) as cathode that uses oxygen directly from the air. A schematic of a GDE is shown in Figure 2-2. It consists of an electrically conductive, porous gas diffusion layer that is hydrophobic, which means it allows air to pass through but prevents leakage of water. The liquid-facing side of the gas diffusion layer is coated with a catalyst. Oxygen diffusing in from the air-facing side is reduced at the air/water/catalyst interface.

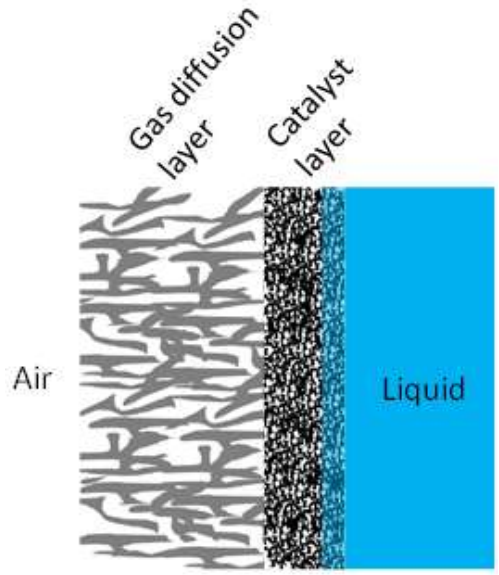

Figure 2-2 Cross section of a gas diffusion electrode.

2.3 Using MFCs as BOD Sensor

There is a relationship between the current or the amount of transferred electrons and the organic matter content in the wastewater since the oxidation of a substrate occurs with the transfer of electrons. The current and total transferred charge is theoretically proportional to the organic concentration. Therefore, MFCs could be another way of measuring BOD concentration with a lower response time than the conventional method.

In Moon et al's MFCs (Moon et al., 2004), the response time of building up a stable relationship between the current and BOD concentration reached to 36±2 min with 25ml volume in each electrode compartment (separated by cation exchange membrane). And the MFCs of 5ml had an even shorter response time, only 5±1 min. But correlation between current and BOD could not be formed when the organic matter concentration is too small. In Kang et al's research (Kang et al, 2003), the correlation could not be shown since the current was too low, 0.01mA with 5mg/L COD. A MFC BOD sensor with a response time of 30 min was developed by Kim et

al, correlating the amount of coulombs with BOD concentration (Kim et al, 2003).

In this thesis project, the BOD sensor was designed as a single chamber MFC with a GDE catalyzed by nanoparticles. In this case, the medium can be fully mixed, avoiding the pH problems. The BOD concentration was correlated to the total transferred charge so that theoretically there should be no limitation on the measurable concentration range. An input voltage was applied to increase the reaction rate so as to reduce the response time.

2.4 Applications

As illustrated above, MFCs can utilize degradable biomass in wastewater to recover renewable energy and control pollution. If MFCs were scaled up and applied in WWTPs, power required for the treatment operations could be partly covered by the produced energy. Moreover, bacteria used in MFCs are self-replicating and thus the catalysts for chemical reactions are self-sustaining (Logan, 2007), which will lower the operation cost.

The amount of transferred electrons is related to the amount of electron donors, or biodegradable organic matters in other words. As a result, it could be deduced that there is a relationship between BOD in wastewater and the electrons it produces. Traditionally, to determine BOD concentration requires five to seven days, but with MFCs, if the response time for current changes is short enough the required time might be cut down to several hours or minutes.

Another potential application of MFCs technology is to monitor the wastewater toxicity. Bacteria could be killed or inhibited with the sudden increase of the poisonous pollutant in the wastewater. Thus, the electric current, or current signal read from voltammeter, might be lowered immediately.

Materials and Experimental Setup

3.1 Instruments and Methods for Analysis

Potentiostat

A potentiostat is an essential electrochemical instrument that is used to control the voltage difference between electrodes.

The potentiostat is normally operated in an electrochemical cell with three electrodes, a working electrode, a reference electrode and a counter electrode. The *Working Electrode* is the electrode where the potential is controlled and the current measured (Gamry website). It can be the cathode or the anode in cases of MFC analysis. *Reference Electrode* is used to measure the working electrode's potential. It should have a constant electrochemical potential, *e.g.*, the silver/silver chloride (Ag/AgCl) electrode with a potential of +0.197V against the normal hydrogen electrode (NHE) or the saturated calomel electrode (SCE) with a potential of +0.242V against NHE. The *Counter Electrode* completes the cell circuit. Generally, the current flows into the system through the working electrode and leaves via the counter electrode. A potentiostat allows analyzing the system under a controlled condition by setting the current or the potential at a defined value (Logan, 2007). A simplified schematic of a potentiostat (Gamry instrument's potentiostat) is shown in Figure 3-1.

The potentiostat can also be used for studying both the cathode and anode or measuring ohmic resistance with only two electrodes set in the system. In this case, the working electrode is connected to the cathode and both the counter electrode and reference electrode are connected to the anode.

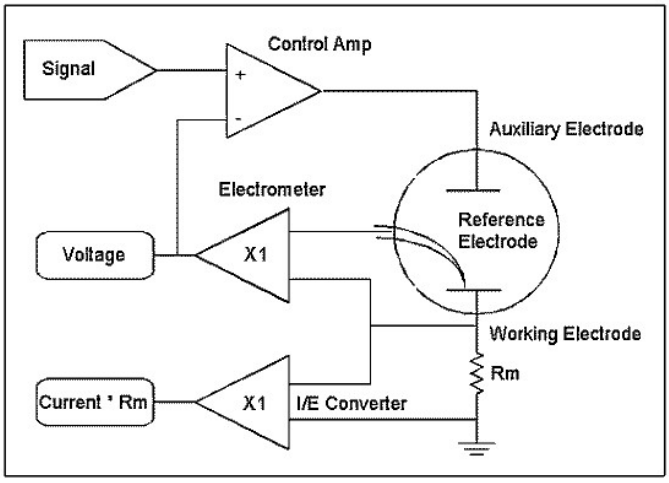

Figure 3-1 A simplified schematic of a Garmy instrument's potentiostat (Garmy website).

Voltammetry tests (CV, LSV)

Voltammetry is a type of potentiodynamic electrochemical measurement which studies the current as the function of applied voltage. It can be used for analyzing the electrochemical activity of microorganisms for example in MFCs, or testing new cathode materials, etc. A potentiostat is required to control the potential of the working electrode that is varied at a certain scan rate. There are two basic types commonly used in MFC experiments, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) (Logan, 2007). When the scan of electrode potential goes in only one set direction, it is referred to as LSV; and for CV, the potential will be continuously scanned in the reverse direction and returns to the starting point. Linear sweep voltammetry and cyclic voltammetry's potential waveform and a typical cyclic voltammogram are shown in Figure 3-2.

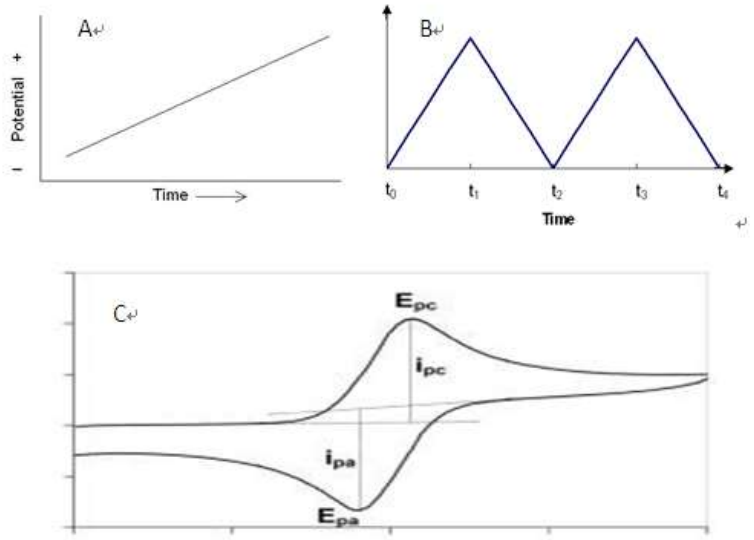

Figure 3-2 (A) Linear sweep voltammetry potential waveform. (B) Cyclic voltammetry potential waveform. Potential is varied as a function of time. (C) Typical polarization curve of cyclic voltammetry (Wikipedia). E_{pc} and E_{pa} show the oxidation and reduction peaks of the redox active compounds. Currents referred to oxidation processes are recorded positive and those recorded negative in the reduction processes.

3.2 Investigation of Gas-diffusion Cathodes

3.2.1 Electrochemical reactor

A schematic of the experimental setup is shown in Figure 3-3. The setup consists of two compartments separated by a cation exchange membrane (CMI-7000, Membranes International Inc.). The volume of each compartment is around 90ml (3cm*3cm*10cm).

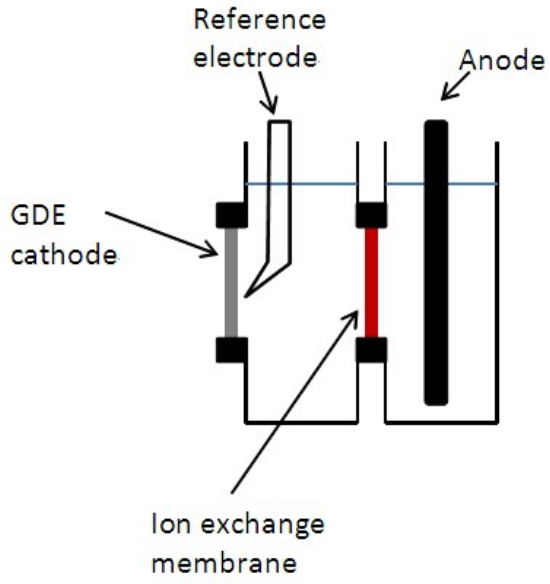

Figure 3-3 The schematic MFC experimental setup.

A gas diffusion electrode (GDE) was used in the cathode compartment. The basic layer of GDE was made by Toray carbon fiber paper TGP-H-060. The air-facing side of the carbon paper was painted with 40% PTFE (Polytetrafluoroethylene) solution. The liquid-facing side was painted with a catalyst mixed with PTFE. On the air-facing side, the hydrophobic PTFE layer was added to prevent liquid leakage through the cathode. On the liquid-facing side, the PTFE acts as glue, binding the catalyst to the carbon paper. PTFE has a melting point of 327°C, so the carbon paper was heated to 350°C for about 30 min to fix the PTFE to the paper. Three types of GDEs were prepared (shown in Figure 3-4),

1. Plain carbon paper without any catalyst coating.
2. Carbon paper coated with carbon nanoparticles (Black Pearls 2000, Cabot Corporation). The carbon paper was painted with carbon nanoparticles and 15% PTFE (wt. PTFE/wt. C). 1.5mg carbon was used per cm^2.
3. Carbon paper coated with platinum loaded activated carbon powder. The platinum powder was 1% Pt on activated carbon. The preparation of the carbon paper coated with Pt was the same as that coated with carbon nanoparticles.

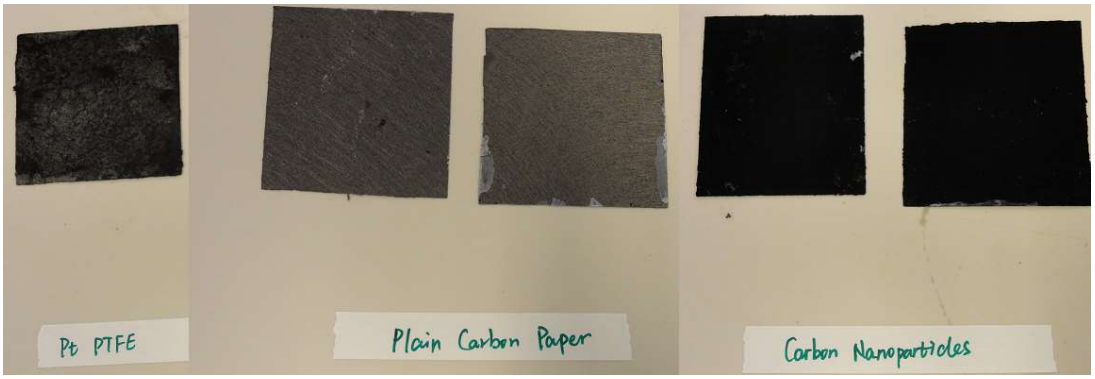

Figure 3-4 The three types of GDEs that were used in the experiment.

The active region of the gas-diffusion electrode, i.e., the area that was exposed to air and the liquid solution, was circular with a diameter of 3cm and a surface area of 7.1cm^2. A steel wire mesh (3cm*12cm) was pressed against the air-facing side of the GDE to transfer electrons to the external circuit.

A graphite rod (Alfa Aeasar) was applied as anode with a diameter of 0.615cm and 8cm length immerging into the medium.

The reference electrode was an Ag/AgCl electrode with a constant potential of +0.2 VS NHE (Bas Inc.).

Some experiments were also carried out with a graphite rod cathode. A 7.1cm^2 area of the rod was coated with carbon nanoparticles the same way as the second GDE. The rod cathode was used to analyze the effect of varying DO concentration in the catholyte (see Figure 3-5).

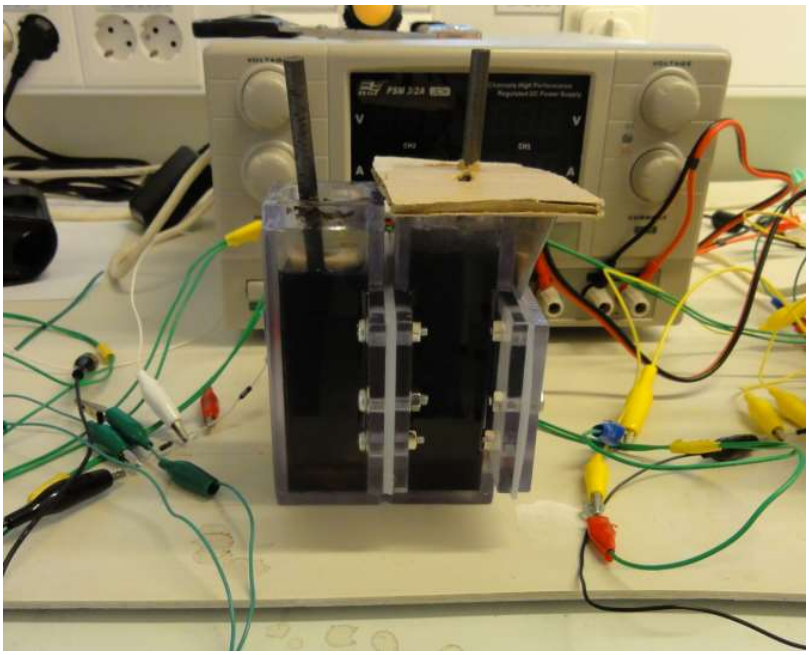

Figure 3-5 MFC with rod cathode.

3.2.2 Operation for GDE properties

GDE properties with different materials and mediums

The performance of the gas-diffusion cathodes was investigated using cyclic voltammetry (CV). CV scans were performed using a potentiostat (KP07, Bank IC, Germany). An external signal was fed to the potentiostat using a PC with LabView software and a data acquisition device (USB-6211, National Instruments). The data acquisition device was also used for logging data. The cathode was connected as the working electrode and anode as counter electrode. An Ag/AgCl reference electrode was also placed in the cathode chamber. The scan rate was 20mV/s from the initial equibilium cathode potential to -0.3 VS NHE. 3 cycles for each CV test were performed and data from the second cycle was used for analysis. The MFC and potentiostat were connected as in Figure 3-6.

First, CVs were run for all three types of GDEs with cathode medium. Then the first and second GDEs were tested with the addition of 28ml filtrate from bacteria culture in the cathode compartment. After the second CV test, 100ml bacteria culture was applied as electrolyte in cathode and the CV tests were made every other week. During the time interval, MFCs were incubated under approximately 0.5mA external current. 20ml culture was changed with cathode medium every two to three days for both cathode and anode compartment.

The bacteria (activated sludge) was collected from Rya WWTP, Gothenburg Sweden, and was cultivated in a 500ml flask with gentle stirring. 100ml medium was changed with cathode medium every other day. The composition of the medium is shown in Table 3-1.

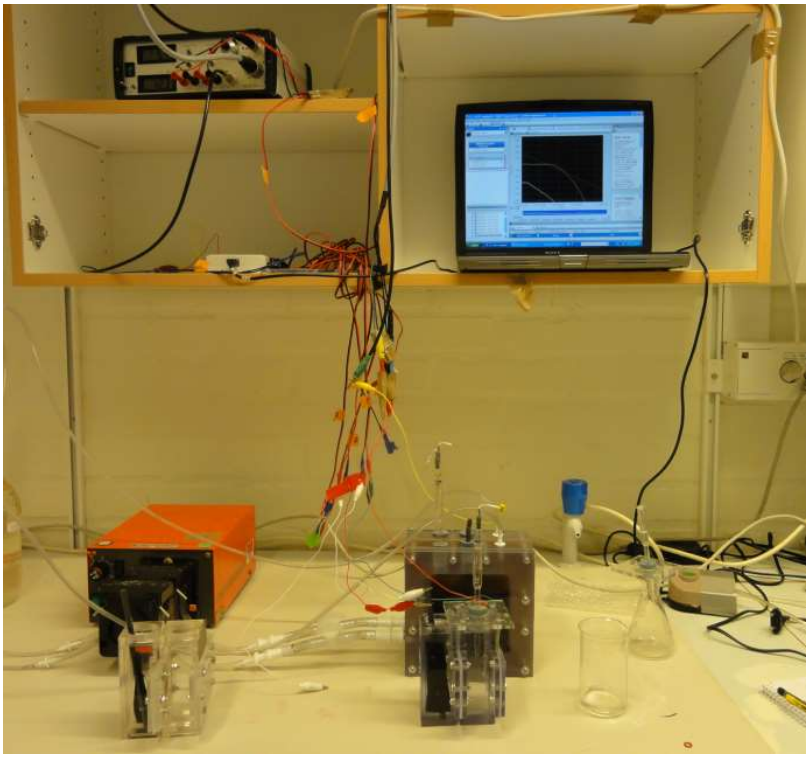

Figure 3-6 Connection of MFCs, potentiostat and normal PC for CV tests.

GDE properties under different DO conditions

The cathode medium was injected with air and nitrogen gas for 5min to establish a saturated and practically no oxygen condition respectively. Together with the normal condition (DO equals to 5.5-6.0mg/L approximately), three CV tests were performed for 1) GDE coated with Pt powder 2) GDE coated with nanoparticles and 3) MFC with rod cathode. The last two tests were done under the catalysis of bacteria.

To compare the different types of bacteria's catalysis, the anaerobic sludge culture was introduced. The culture was applied in both cathode and anode compartment. Tests were performed for both paper cathode with nanoparticles and rod cathode. Another round of CV tests was made after one week's incubation.

3.3 Investigation of Using a MFC as a BOD Sensor

3.3.1 Big MFC construction

A single chamber MFC was constructed as shown in Figure 3-7.

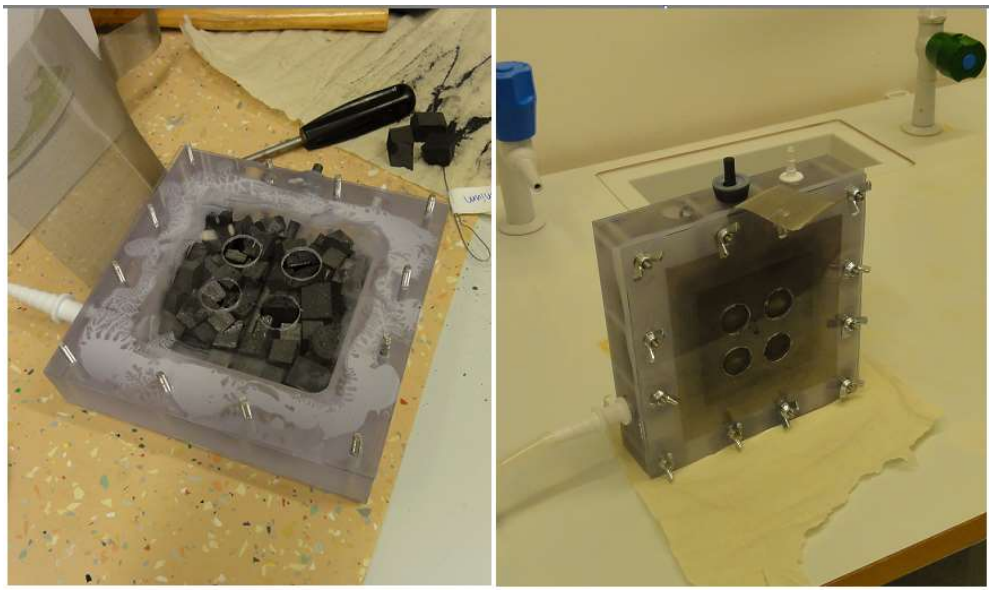

Figure 3-7 Construction of the single chamber MFC.

The construction of single chamber MFC is similar to two chambers MFC except for the lack of ion exchange membrane. Instead, a Wettex cloth was used to separate the anode and the cathode. Rod and graphite pieces (1cm*1cm*1cm) were used for anode. The area of the electrode that was exposed to air and the liquid solution was 4 circles with a diameter of 2cm and the total surface area was 12.6cm^2. Bacteria and medium (see Table 3-2) with adjusted acetate concentration were used for the MFC. The liquid volume of this MFC is approximately 180ml (total compartment was 3cm*10cm*10cm).

3.3.2 Operation for BOD sensor

MFC was first filled with 180ml bacteria culture and then connected to medium loop that the anode medium was continuously pumped into the MFC chamber. The bacteria were incubated for about one month before the tests started to get a better bioelectrochemical activity.

During the tests, MFC was operated under two conditions, with 100ohm external resistance and under an input voltage (1V) for accelerating the reactions. A Gamry Series G750 potentiostat was applied to control the cell voltage with the anode as working electrode. Logged data was collected by the USB-6211 data acquisition device.

For both types of operational conditions, anode medium (see Table 3-2) with 0.5mM, 2mM and 4mM of acetate was used as electron donor. Five days of incubation was performed under each acetate concentration. The total transferred charge could then be calculated based on

the logged current data.

Table 3-1 Composition of the medium for testing GDEs properties and the bacteria's culture.

Preparations		**Cathode Medium**
$NaHCO_3$*		840 mg/L
CH_3COONa*		3280 mg/L
KH_2PO_4		5281 mg/L
K_2HPO_4		10661 mg/L
Mineral salts (mg/L)		100 ml/L
NaCl	29250	
$MgSO_4*7H_2O$	1000	
$CaCl_2*2H_2O$	1000	
NH_4Cl	1000	
Trace elements #1 (mg/L)		1 ml/L
$FeCl_2*4H_2O$	2000	
H_3BO_3	50	
$ZnCl_2$	50	
$CuSO_4$	30	
$MnCl_2*4H_2O$	500	
$Al_2(SO_4)_3*18H_2O$	50	
$CoCl_2*6H_2O$	50	
$NiCl_2$	50	
HCl concentrated	1ml	
Trace elements #2 (mg/L)		1 ml/L
Na_2SeO_3	100	
$Na_2WO_4*2H_2O$	50	
Yeast (mg/L)		10 ml/L
Yeast extract	1000	

*For the cathode chamber, $NaHCO_3$ was used while CH_3COONa was not added, and for the anode chamber and bacteria culture, CH_3COONa was added instead of $NaHCO_3$.

Table 3-2 Composition of the medium for BOD sensor.

	Anode medium (mg/L)
NaCl	2925
$MgSO_4*7H_2O$	100
$CaCl_2*2H_2O$	100
NH_4Cl	100
$NaHCO_3$	0
CH_3COONa*	*
Yeast extract	10
KH_2PO_4	3879
K_2HPO_4	12455

Trace elements (1 ml/L)	
$FeCl_2*4H_2O$	2000
H_3BO_3	50
$ZnCl_2$	50
$CuSO_4$	30
$MnCl_2*4H_2O$	500
$(NH_4)Mo_7O_{24}$	50
$AlCl_3$	50
$CoCl_2*6H_2O$	50
$NiCl_2$	50
HCl concentrated	36%, 1 ml
Na_2SeO_3	100
$Na_2WO_4*2H_2O$	50

***Varied during the tests.**

Results and discussion

To make the results clear, a detailed explanation of notations used in all figures is shown in Table 4-1.

Table 4-1 Detailed explanation of notations in figures.

Notations	Explanation
plain	gas-diffusion electrode with plain carbon fiber
nano	gas-diffusion electrode coated with carbon nanoparticles
Pt	gas-diffusion electrode coated with Pt powder
GDE	gas-diffusion electrode
rod	rod electrode as cathode
no catalyst	cathode medium without bacteria or filtered bacteria culture
filtrate	cathode medium with filtered bacteria culture
bacteria	cathode medium containing bacteria enriched from activated sludge
oxic culture	using aerobic bacteria culture as catholyte
anaerobic sludge	using anaerobic sludge as catholyte
1st	one-week's cultivation after addition of the bacteria or sludge
2nd*	two-week's cultivation after addition of the fresh bacteria and medium
mM	adjusted concentration of acetate, mmol/L
min	operation time of the BOD sensor, min
linear	linear relationship of the total charge under each acetate concentration

*After two-week's incubation of the MFCs, the pH value in the cathode chambers reached up to 9.5, both with plain carbon fiber electrode and nanoparticles coated electrode, which is too high for bacteria. Therefore, the cathode chambers were washed and filled with fresh bacteria and cathode medium. Tests were made two weeks after replacing the catholyte.

4.1 Oxygen reduction on gas-diffusion electrodes

4.1.1 Comparison between materials and catalysts

A comparison of the three tested GDE materials' performance is shown in Figure 4-1. The tests were run without bacterial catalysis. It is clearly seen that the performance of the GDE coated with nanoparticles was slightly lower than the Pt-catalyzed cathode, whilst supplied a much higher current than the plain carbon fiber GDE. This current difference is probably because of the considerably larger contact surface area that is produced by nanoparticles. The surface area of the nanoparticles is calculated as follows,

$$\mathrm{A} = 1.5\frac{\mathrm{mgC}}{\mathrm{cm^2}} \times 7.1\mathrm{cm^2} \times 1485\frac{\mathrm{m^2}}{\mathrm{g}} = 15.8\mathrm{m^2} \qquad 4\text{-}1$$

where 1.5mgC/cm^2 is the density of the nanoparticles used on the carbon paper; 7.1cm^2 is the cathode's exposure area to air; 1485m^2/g is the surface area of the carbon nanoparticles (Carmo et al., 2007).

Moreover, the increase of electrode surface area will also lower the current density and thus lower the activation losses (Freguia et al., 2007). Pt powder has a better catalysis than nanoparticles.

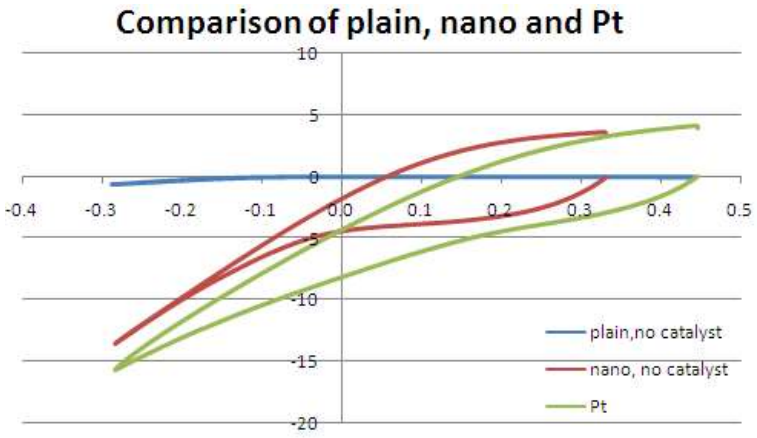

Figure 4-1 Comparison of GDEs' performance without bacterial catalysis. Current (mA) is plotted against the cathode potential (V). All the potentials are presented with respect to NHE.

In Figure 4-2, CVs were made when bacteria are cultivated for one week after added into the system. The nanoparticle coated GDE still performed much better than the plain carbon electrode. As a result, plain carbon fiber gas-diffusion electrode is not suitable for MFC because of its smaller surface area for electron transfer and bacteria's adhesion.

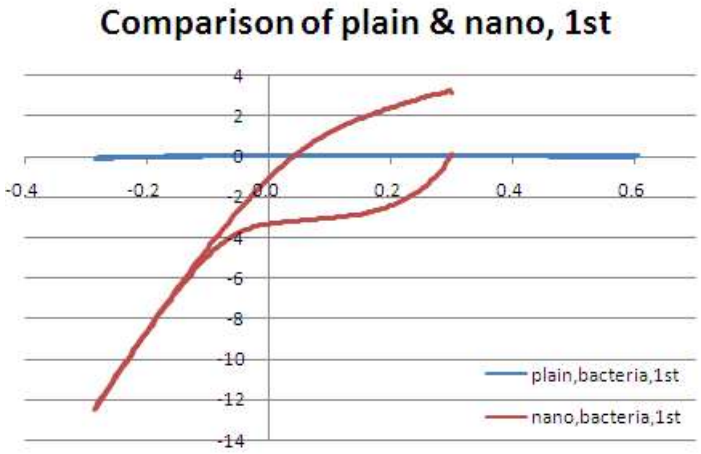

Figure 4-2 Comparison of two GDEs' performance with bacterial catalysis. Current (mA) is plotted against the cathode potential (V). All the potentials are presented with respect to NHE.

To investigate whether bacteria can improve the cathode performance, tests of GDEs under different cathode medium conditions were made (see Figure 4-3).

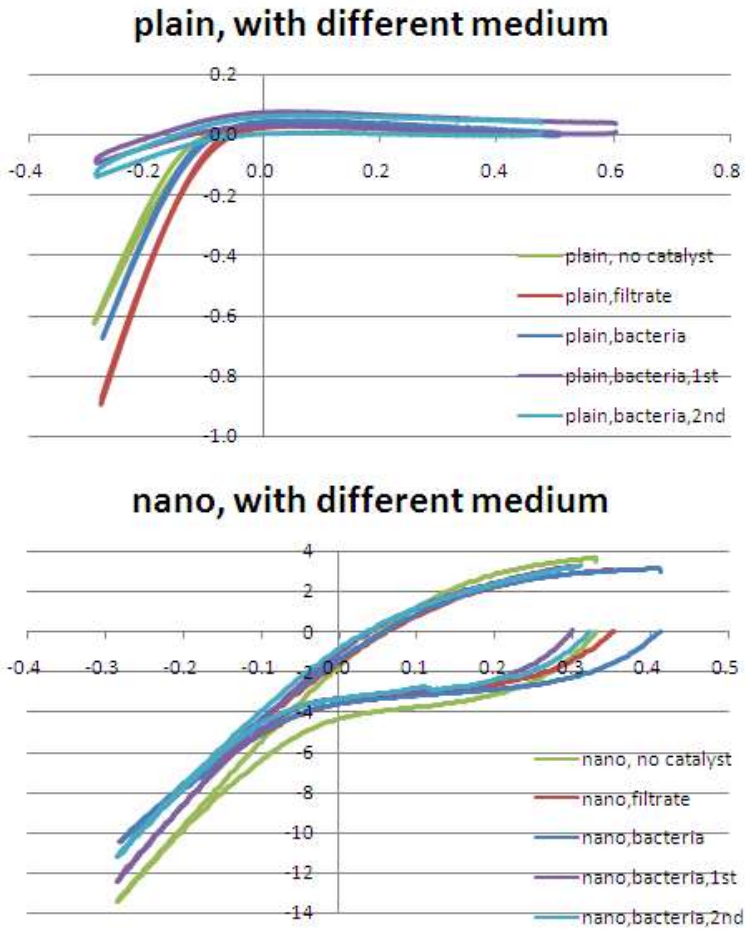

Figure 4-3 Comparison of the GDEs' performances under different cathode medium conditions: without bacteria catalysis (-no catalyst), with bacteria's metabolite (-filtrate), and with bacteria existing in the system(-bacteria, -1st, -2nd). Current (mA) is plotted against the cathode potential (V). All the potentials are presented with respect to NHE.

In the upper figure, the performances of the plain carbon fiber GDE remain almost the same before and after bacterial participation. But after the bacteria are cultivated for one and two weeks, there is a significant current decrease. For the GDE coated with carbon nanoparticles (in the lower figure) cathode performance did not differ much under all circumstances. Both GDEs tests show a different result than other research that applied rod cathodes. Cournet et al. found out that the cathode performance will be greatly improved after one hour of adding bacteria (Cournet et al., 2010a and Cournet et al., 2010 b). In Zhang et al's experiment, the MFC's performance began to increase after two-days of operation, with the observation of microbial cells growing on the cathode. It suggests that the bacteria can catalyze the oxygen reduction reaction (Zhang et al., 2008). Rabaey et al. also concluded that bacteria will reduce the overpotential losses and improve cathode performance (Rabaey et al., 2008).

Comparing the differences between the experiments in the thesis project with those in the articles, following interpretation might explain the different result:

pH value in the cathode compartment will be continuously increased during the cultivation as

protons are consumed and cations are transferred from the anode compartment. In this experiment, the cathode medium was partly replaced (20ml out of 100ml) every other day or every three days. It is comparatively longer than experiments above (one hour, two days and one day, respectively). The electrochemical test was made after one week and two weeks after the bacteria's participation. The initial pH value when the bacteria were first added was about 7.1. It rose to about 7.5 after 2 day's cultivation. Two weeks after addition of bacteria, a mistake was made that the system was continuously cultivated for 6 days without changing catholyte and the pH value was increased to 9.5. Thus, the lack of bacterial catalysis after two weeks of incubation may have been caused by the increase in pH in the cathode chamber. However, bacterial inactivation by increased pH does not explain the lack of bacterial catalysis seen in the CV tests done with the addition of filtrate, bacteria, or bacteria after one week incubation.

A disinfection chemical, H_2O_2, can be produced as intermediate product (see chemical reactions in Chapter 2.1 or Table 2-1) in the cathodic reduction of oxygen. Especially on carbon cathodes, H_2O_2 can accumulate to high concentrations. A bioelectrochemical system can be used to produce concentrations of H_2O_2 reaching several thousands of mg/L with a low input of electrical energy (Modin and Fukushi, 2011). During the incubation of the reactor, it was operated at a constant current of approximately 0.5mA, which means 0.32mg/h of H_2O_2 could theoretically have been produced at the cathode surface. In addition, bacteria can produce quinones and heme-containing groups, which might catalyze oxygen reduced to H_2O_2 (Freguia et al., 2010). This together with an increased pH value may have prevented bacteria from improving the catalytic properties of cathode during the incubation.

Thirdly, the lack of effective contact surface area between cathode and bacteria might also lead to an inefficient electrocatalysis. The dimension of carbon nanoparticles is always smaller than 100nm, whereas a bacterial cell usually ranges from 0.2-2 micrometers in width or diameter and up to 1-10 micrometers in length. Therefore, as illustrated in Figure 4-4, despite the electrochemical area of the nanoparticles was 15.8 m^2, the actual contact surface area between bacteria and nanoparticles might only be a small fraction of the surface area actually available for oxygen reduction.

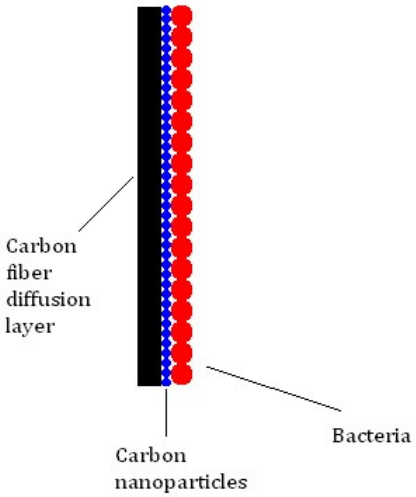

Figure 4-4 Schematic of the carbon fiber diffusion layers coated with nanoparticles.

Moreover, on GDEs oxygen comes directly from air and reacts on the surface of carbon in the air/water/electrode interface. Bacteria are present in the water and may not have much influence on the reaction if they are spatially separated from the place where oxygen reduction occurs. Indeed, bacteria on GDEs may even aggravate the activation and transportation losses, and thus increases the cathode overpotential. This seemed to occur on the plain GDE, which showed a worse performance after one- and two-weeks incubation.

Although bacteria did not improve catalysis, Figure 4-2 shows that the GDE coated with nanoparticles exhibited a stable performance after incubation for two weeks in the presence of bacteria. So, it could be suitable for single-chamber MFCs in which the wastewater and microorganisms are in contact with the cathode. Maybe the H_2O_2 that is generated on the surface helps to keep the surface of the nanoparticles clean. Plain cathodes, however, showed worse performance.

A comparison between the performance of bacteria and platinum as cathode catalysts is shown in Figure 4-5.

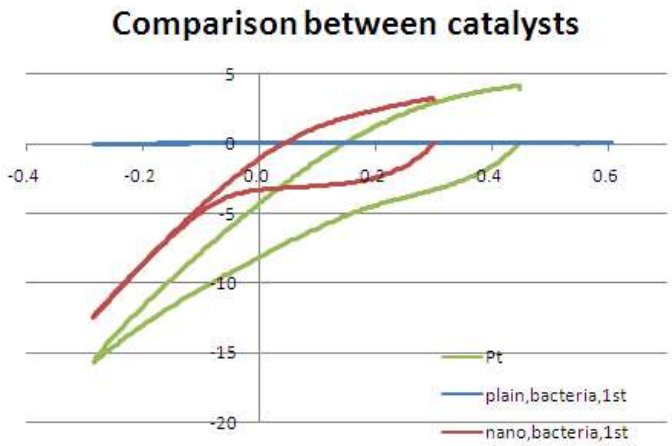

Figure 4-5 Comparison between the performance of platinum and bacteria as cathode catalysts. Both plain carbon fiber diffusion layer and carbon nanoparticle GDE are tested with bacteria

catalysis after one-week's cultivation. Current (mA) is plotted against the cathode potential (V). All the potentials are presented with respect to NHE.

A clearly higher current and cathode potential is reached on the GDE that is coated with Pt powder. Yet, the performance of carbon nanoparticle GDE is not far behind. As discussed above, bacteria's catalysis on GDEs might be hindered by the culture environment; it might therefore be possible to enhance its cathode performance approaching to Pt-catalyzed cathode by e.g., adjusting experiment operation or controlling accumulation of intermediate production.

4.1.2 Comparison under different DO conditions

In this chapter, only the properties of the GDE with nanoparticles was analyzed, as the plain fiber GDE is proved to have a negligible performance compared with the other GDEs (see chapter 4.1.1).

A comparison of the cathodes performance under three DO conditions is shown in Figure 4-6. The result (B in Figure 4-6) suggests that the rod cathode efficiency does not differ much with DO level changes, producing an identical maximum current even when DO value drops to 0. In theory however, when applying rod cathode in MFCs the level of dissolved oxygen is an important restraining factor to the cathodic performance (Cournet et al., 2010a). Our experiment was conducted with the catholyte exposed to air, so oxygen may have dissolved into the water during the CV runs. It should also be noted that CV is a dynamic test, so non-faradaic current will contribute to the measured current levels. The equilibrium potential at the start of each scan decreased from 0.32V under oxygen-saturated conditions to 0.15V under zero-oxygen conditions.

The GDEs generated a higher current than the rod electrode. The reduction rate of oxygen on the GDE at the maximum current can be calculated. The maximum produced current density (i_{max}) when DO=0 at the rod electrode is 10.5 A/m^2. 4mol electrons are transferred by the reduction of 1mol O_2. So, the oxygen's reduction rate is calculated as follows (not taking non-faradaic currents into account),

$$\mathrm{R_{DO=0}} = \frac{\mathrm{i_{max}}}{4\times \mathrm{q_{e^-}}\times \mathrm{NA}}\,\mathrm{mol\ O_2/(s\cdot m^2)} = 0.27\times 10^{-4}\,\mathrm{mol\ O_2/(s\cdot m^2)} \qquad 4\text{-}2$$

where $\mathrm{q_{e^-}}$ is the electric quantity of one electron which equals to 1.6×10^{-19}C, and NA is Avogadro's number which equals to $6.02\times 10^{23}/\mathrm{mol}$.

The maximum oxygen penetration rate through the gas-diffusion paper can be calculated based on data given from the manufacturer. The theoretical oxygen penetration rate is calculated as follows,

$$\mathrm{R_{theory}} = \frac{1900\frac{\mathrm{mL\cdot mm}}{\mathrm{cm^2\cdot h\cdot mmH_2O}}\times 10.36\frac{\mathrm{mH_2O}}{\mathrm{1atm}}\times 0.21\mathrm{atm}}{0.19\mathrm{mm}\times 24.5\frac{\mathrm{mL}}{\mathrm{mmol}}}^{2} = 2467\,\frac{\mathrm{mol}}{\mathrm{m^2\cdot s}} \qquad 4\text{-}3$$

where 1900mL*mm/cm^2*h*mmH_2O is the gas permeability on the carbon fiber paper; 0.19mm is the thickness of the paper; 10.36m is the atmospheric pressure calculated as water column; 0.21 is the percentage of oxygen in the air; and 24.5ml/mmol is the gas molar volume under 1atm.

The oxygen reduction rate is much less, 8 order of magnitudes lower than its theoretical maximum penetration rate. Therefore, it could be presumed that oxygen's penetration through the gas-diffusion paper rate is probably not limiting for the cathode performance.

Similarly, when oxygen is saturated, the reduction rate is still $0.27 \times 10^{-4} \mathrm{mol\ O_2/(s \cdot m^2)}$. As a result, the oxygen's penetration rate seems to be constant, not affected by the medium's DO condition. A similar result was obtained between the GDE catalyzed coated with nanoparticles and with platinum powder (A and C in Figure 4-6).

Comparison between GDE and rod electrode shows that rod is less efficient than the paper cathode probably because it is not directly in contact with air but is more affected by liquid-phase DO concentration. The equilibrium potential (i.e., when current is zero) varies with DO concentration for the rod, but not so much for the GDE.

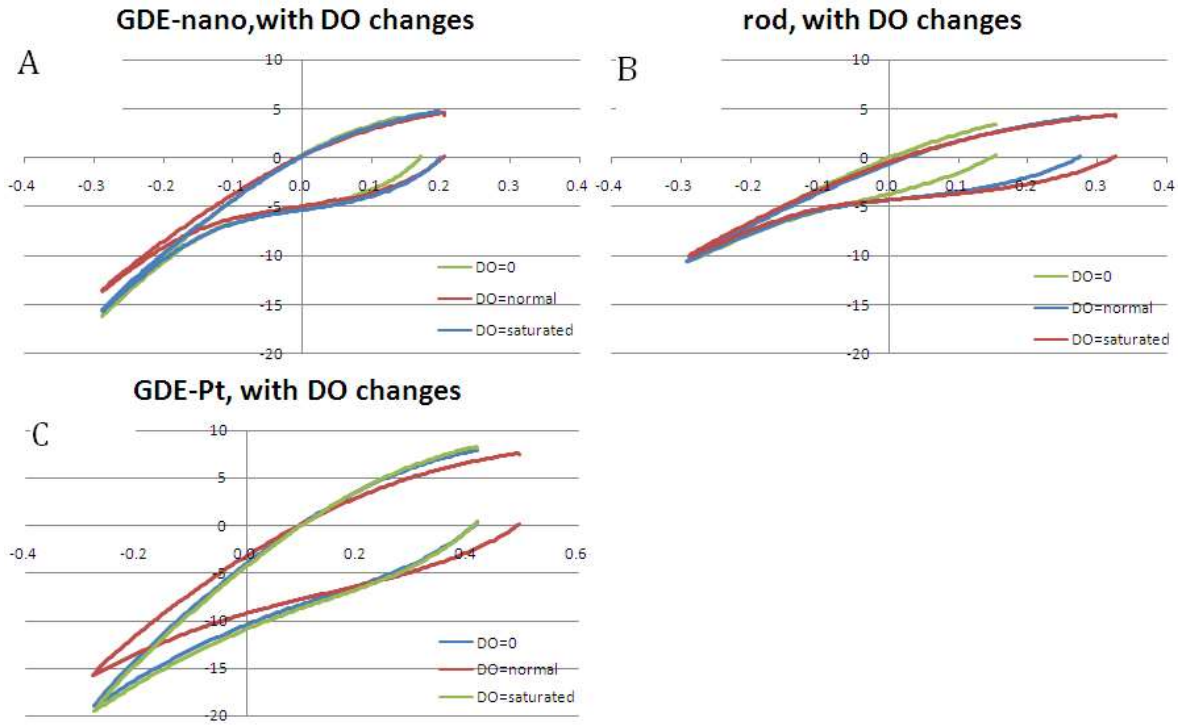

Figure 4-6 Comparison of the cathodes performances with DO changes. The normal dissolved oxygen value is around 5.5-6.0 mg/l. Current density (A/m^2) is plotted against the cathode potential (mV). All the potentials are presented with respect to NHE.

Figure 4-7 shows the current productivity difference with the change of cathode culture. Two cultures were tested. The first was aerobic and had been cultivated in the lab with acetate as carbon source. The second was anaerobic and was collected from the anaerobic digester in Rya WWTP. The current density decreases sharply after introducing anaerobic sludge in the

cathode compartment. Combining the results above that no improvement is made by bacteria and the DO level will not affect the cathode performance, it might conclude that anaerobic bacteria are not suitable for catalyzing oxygen reduction. Large amount of oxygen that penetrates from the gas diffusion layer might inhibit the bacteria's activity. Adsorption of metabolites of the anaerobic bacteria may even prevent the electrochemical reaction so that the cathode performance is even lower than without any bacteria addition. Furthermore, the anaerobic sludge was not diluted, and the high sludge concentration might be the reason. This needs to be further analyzed.

The figure also indicates that even with thick anaerobic sludge in cathode compartment, the cathode performance still seemed to be relatively high after one-week's incubation.

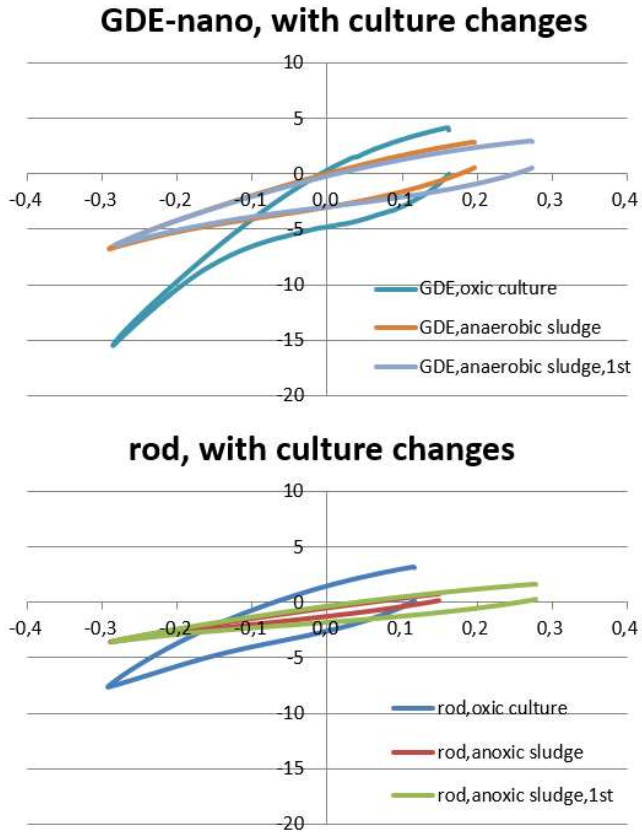

Figure 4-7 Comparison of the cathodes performances with different culture. Current density (A/m^2) is plotted against the cathode potential (mV). Potentials are calculated respect to NHE.

4.2 Using a MFC as BOD sensor

Chapter 4.1 shows that carbon nanoparticle GDE has relatively stable performance even in the presence of bacteria. Therefore, it could be suitable for single-chamber MFC, which is used in this experiment as a BOD sensor. However, it gives worse performance than the cathode coated with Pt. Actually, in a BOD sensor a stable performance is more required other than good performance. Moreover, a sensor does not necessarily have to be operated as an MFC

(i.e., with energy output). Instead, an input voltage could be introduced to drive the reaction at a higher rate. Therefore, in this chapter, a single-chamber MFC operated under a 100ohm external resistance and under an input voltage were tested for measuring BOD values. BOD value was reflected by the concentration of acetate. A solution with known concentration of acetate (i.e., BOD) was fed to the MFC and the current was monitored over time. Figure 4-8 shows an example of current as a function of time.

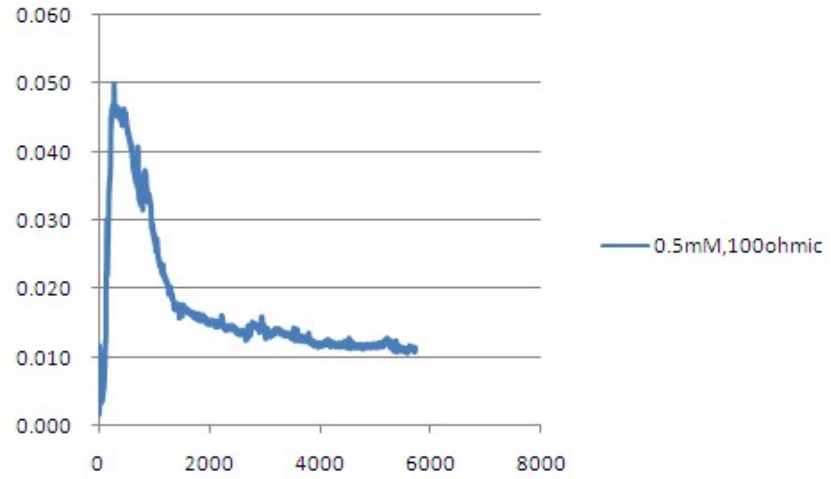

Figure 4-8 Current (mA, y-axis) as a function of time (min, x-axis) with 100ohm external resistance under 0.5mM acetate.

As the amount of electrons transferred is theoretically proportional to the organic matter content in the wastewater, the total charge production against time by the MFC under 100ohm resistance is plotted in Figure 4-9. It can be seen that a shorter time is needed for the curve to be stable with less BOD concentration. So, in reality, the response time of a BOD sensor depends on the concentration of BOD.

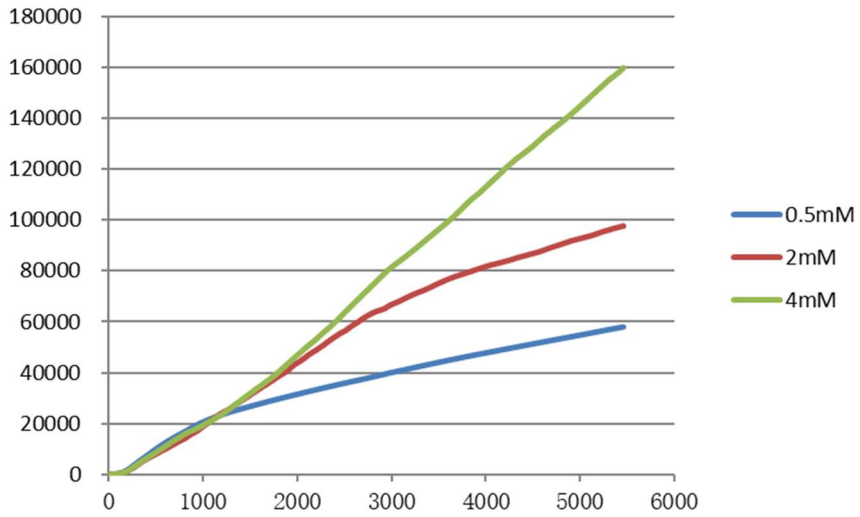

Figure 4-9 Total charge production (mC, y-axle) under different acetate concentrations under 100ohm resistance. Total charge is plotted against time (min, x-axle).

Relationship between acetate concentrations and total transferred charges by MFC under

100ohm resistance is shown in Figure 4-10.

A linear relationship appeared after 4800 minutes (approximately 3.5 days) of incubation, which means that at this time spot, the MFC's total transferred charge can be used to reflect the BOD value for the tested range. BOD value can be calculated from the total transferred charge by using this linear relationship. In theory, there will be no electron transferred without acetate presence in the system, which is different from the result in Figure 4-9. This might be because the bacteria can be able to use other energy sources, i.e., the dead bacteria. Therefore, the BOD sensor's accuracy in reality needs to be more tested and calibrated.

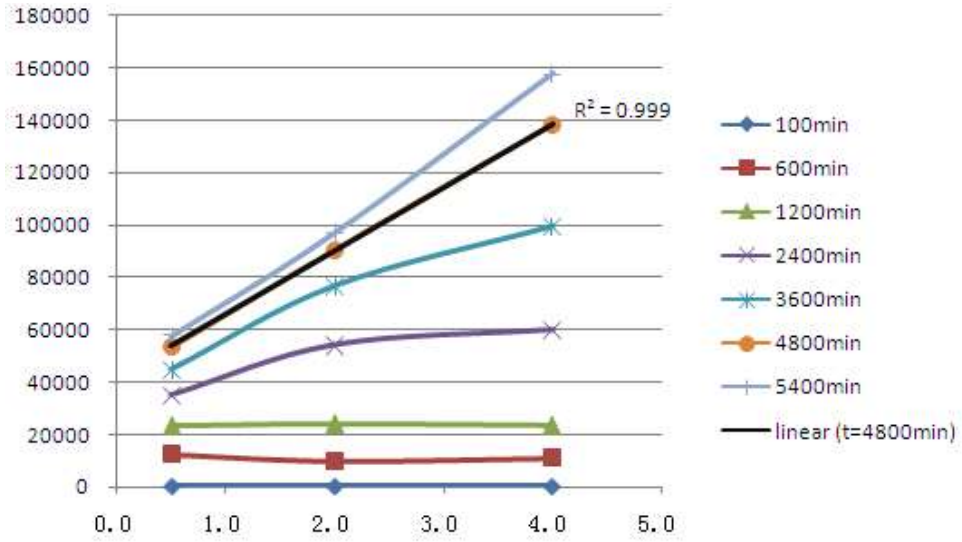

Figure 4-10 Relationship between acetate concentrations (mM, x-axle) and total charges transferred by real MFC under 100ohm resistance (C, y-axle). Different time spots are picked from 100min after incubation.

The rate of the MFC's performance can be even higher when inputting an external voltage. Figure 4-11 shows that with the control of the cell voltage, after only 1800 minutes (1.25 days), the total charge of the MFC can be used to reflect the BOD value. As a result, comparing to the 5-7 days conventional way of measuring BOD values, using MFCs as BOD sensor is more convenient and time saving.

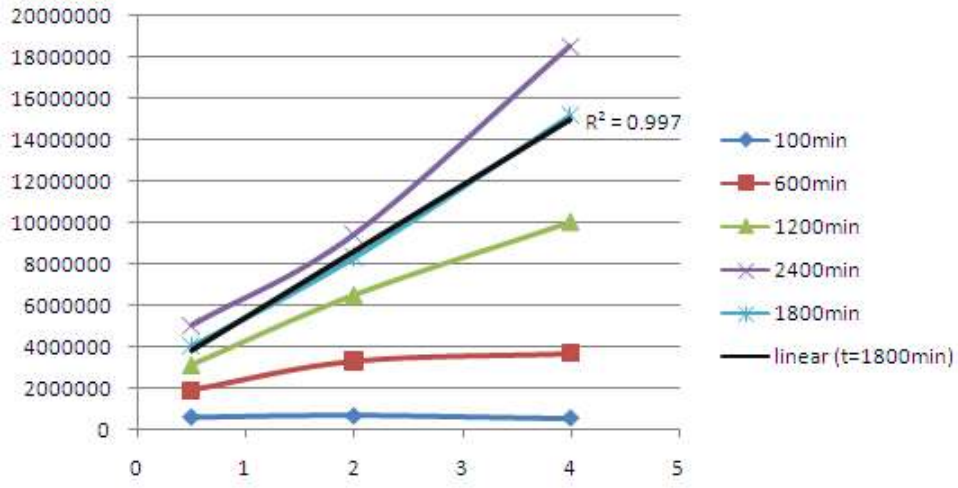

Figure 4-11 Relationship between acetate concentrations (mM, x-axle) and total charges transferred by real MFC under 1V input voltage (C, y-axle). Different time spots are picked from 100min after incubation.

Conclusion and recommendation

5.1 Conclusion

The performance of the plain carbon GDE is much worse than the GDE coated with nanoparticles. This is probably due to the increase of contact area that is produced by nanoparticles. Pt showed the best performance before addition of bacteria.

The bacteria showed no catalysis function on both GDEs. Compared with other research, it could be surmised that the bacteria's activity might be inhibited by the over increased pH value in cathode chamber and the accumulated H_2O_2 production. The lack of effective surface area between cathode and bacteria might also lead to inefficient catalysis. Moreover, oxygen might be directly reduced on the GDE's air/electrode/water interface instead of penetrating into the cathode medium; bacteria therefore don't have much influence on the reaction. Further analysis is needed to invesigate these assumptions.

GDE coated with Pt powder gave the best performance of the three types of electrodes. But the performance of carbon nanoparticles GDE is not far behind. The cathode could be possibly enhanced approaching to Pt-catalyzed cathode by e.g. adjusting experiment operation or controlling accumulation of intermediate products.

DO concentrations did not affect the performance of GDEs with nanoparticles and with Pt powder, which further convinced that the oxygen is reduced on the air/electrode/water interface. The performance of rod electrode is more affected by the liquid-phase DO concentration.

The type of sludge will affect the performance of GDE with nanoparticles. The cathode performance was indeed decreased after introducing anaerobic bacteria probably because of its high concentration. However, it is observed that even with thick sludge, the cathode with nanoparticles gave a stable performance with the presence of both kinds of bacteria. The nanoparticles GDE is therefore presumed to be suitable for single-chamber MFCs in which the wastewater and microorganisms are in contact with the cathode.

The single-chamber MFCs can be used for measuring BOD value. It showed perfect linear relationships between total transferred charges and acetate concentration after less than five days incubation. For the MFC loaded with 100ohm resistance, 3.5 days are needed. With an input voltage to accelerate the reaction, the BOD value can be obtained after only 1.25 days incubation. Notice that each MFC needs to be calibrated before using as BOD sensor. A longer incubation time might make the observation value higher than the real value.

5.2 Recommendation

- Gas diffusion electrode coated with nanoparticles is recommended in MFCs for its

relatively high performance and more energy-saving comparing with rod electrode and more economic than Pt-catalyzed GDE.

- Bacteria do not improve the oxygen reduction rate in this thesis study but could be further research with adjusted experimental conditions are needed to definitely conclude whether or not bacteria can catalyze oxygen reduction on GDEs. Anaerobic bacteria are not recommended.
- GDE coated with nanoparticles is suggested in MFC BOD sensor. The measuring time could be shortened using an input energy. A higher current-to-volume ratio would also reduce the measuring time. This could be achieved by increasing the surface area in the reactor. The BOD sensor needs to be carefully calibrated especially when the measurement has a low BOD concentration. To wash and refresh the whole system with zero-BOD medium could probably be a way of reducing the errors when measuring low BOD wastewater.

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