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**Domestic wastewater treatment and electricity recovery by a  
PVDF-based air-cathode MFC coupled with a low voltage  
booster multiplier**



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**This thesis is submitted in partial fulfilment of the requirements for the degree of  
Doctor of Philosophy in Engineering**

**DOCTOR DISSERTATION**

**Domestic wastewater treatment and electricity recovery by a  
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## List of abbreviations

AC	Activated Carbon
ANAMMOX	Anaerobic Ammonium Oxidation
AOB	Ammonium Oxidizing Bacteria
CC	Closed circuit
COD	Chemical Oxygen Demand
D-MFC	Dual Chamber Microbial Fuel Cell
DO	Dissolved Oxygen
DWW	Domestic Wastewater
Electroammox	electroactive anammox
EET	Extracellular Electron Transfer
HRT	Hydraulic Retention Time
$I_D$	current density
LVB	Low Voltage Booster
LVBM	Low Voltage Booster Multiplier
MEC	Microbial Electrolysis Cell
MET	Microbial Electrochemical Technology
MFC	Microbial Fuel Cell
MFC-PVDF/AC	Air-cathode PVDF-based Microbial Fuel Cell
NOB	Nitrite Oxidizing Bacteria
OCP	Open Circuit potential
OCV	Open Circuit Voltage
pCOD	Particulate Chemical Oxygen Demand
$P_D$	Power Density
PMS	Power Management System
Pt	Platinum
PTFE	Polytetrafluoroethylene
PVDF	Poly(vinylidene fluoride)
RE	Reference Electrode
$R_{ext}$	External resistance
RHE	Reference Hydrogen Electrode
$R_{int}$	Internal resistance
sCOD	Soluble Chemical Oxygen Demand
SHE	Standard Hydrogen Electrode
SS	Suspended Solid
SWW	Synthetic Wastewater
tCOD	Total Chemical Oxygen Demand
TN	Total Nitrogen
$V_{out}$	Output voltage
VSS	Volatile Suspended Solid

# List of Publications

Dissertation submitted for the degree

I- Title:

Domestic wastewater treatment by serpentine up-flow MFCs activated carbon air-cathodes coupled with MEC and energy harvesting s using a newly designed Low Voltage Booster and Multiplier (LVB and LVBM)

II- Published paper

**1**-N.J. Koffi, S. Okabe, Domestic wastewater treatment and energy harvesting by serpentine up-flow MFCs equipped with PVDF-based activated carbon air-cathodes and a low voltage booster, Chemical Engineering Journal. 380 (2020) 122443. doi:10.1016/j.cej.2019.122443.

**2**-High voltage generation from microbial fuel cells using a newly designed low voltage booster multiplier (LVBM) (submitted) Manuscript Number: POWER-D-19-03436

**3**- Bioelectrochemical anodic ammonium oxidation in a single chamber Microbial Electrolysis Cell (In preparation, expected to be published).

# Abstract

Title of dissertation submitted for the degree

## **Domestic wastewater treatment and electricity recovery by a PVDF-based air-cathode MFC coupled with a low voltage booster multiplier**

低電圧昇圧増倍器を搭載した PVDF-based air-cathode MFC による都市下水処理および電力回収

Microbial fuel cell (MFC) has emerged as a promising technology during these two-decade due to its ability to simultaneously treat domestic wastewater and to directly produce renewable bioelectricity. However, the high capital cost, low voltage output, and low effluent quality are major obstacles of the practical application of MFCs in wastewater treatment. Therefore, the present study aims to develop a cost-effective and energy-saving MFC system for domestic wastewater treatment. The current status and issues of MFC technology for its practical application are summarized in Chapter 1. This chapter also provides the objectives and outline of this dissertation. **Chapter 2** provides literature reviews about MFC technology applied for domestic wastewater treatment with an emphasis on MFC architecture, operating conditions and, cost-effective anode and cathode materials. This chapter also reviews the existing power management system (PMS) technology used to boost the low voltage output of MFC which is usually ranging from 3 to 12 V. Furthermore, the principle of microbial electrolysis cell (MEC), operating conditions, and current applications are described in this chapter.

In **Chapter 3**, PVDF-based air-cathode MFCs (MFC-PVDF/ACs) were constructed and operated for about 6 months. The performances in terms of COD removal and power production of the MFC-PVDF/ACs were compared with those equipped with platinum-catalyzed air-cathode MFCs (MFC-Pts). Interestingly, MFC-PVDF/ACs achieved higher COD and SS removal and generated higher power densities than the MFC-Pts. In addition, the PVDF-based air-cathode is more durable than Pt cathode. These results suggest that the expensive platinum-based air-cathode is not always necessary for domestic wastewater treatment, and the low-cost PVDF-based air cathode could be used for large-scale MFCs. Although the MFC-PVDF/AC achieved excellent COD and an SS removal, two major issues still remain; the low output voltage and removal of ammonium nitrogen in the treated effluent.

**Chapter 4** focuses on the development of the new low voltage booster (LVB) designed specifically for the low voltage output of the MFC ( $< 0.5$  V). Unfortunately, most of the commercially available PMSs require a startup voltage  $> 0.7$  V which is higher than the working voltages of typical MFCs. In this chapter, a transistor-based LVB system was proposed to harvest electrical energy during the domestic wastewater treatment (ie. COD oxidation) and boosts up the low voltage of the MFC to a usable level (4 - 5.2 V).

In **Chapter 5**, a low voltage booster multiplier (LVBM) was developed to further increase the low voltage output of MFC. In the LVBM electronic system, the low MFC-PVDF output voltage is firstly boosted by a transistor-based DC/AC self-oscillating LVB circuit, and the boosted voltage was further multiplied by a multistage single-phase Cockcroft-Walton voltage multiplier circuit. A LVB with a 20-stage AC/DC multiplier circuit could amplify the MFC voltage (ca. 0.4 V) up to  $89 \pm 22$  V, which was the highest boosted voltage that has been ever reported, for several days without voltage reversal. The feasibility of LVBM application in MFC technology is discussed.

The MFC-PVDF/AC was successfully used to remove COD from domestic wastewater in Chapter 3. However, ammonium nitrogen must be removed from the MFC treated effluent. The conventional

nitrification-denitrification systems require the high-energy demanding aeration and effluent recycling. The ammonium is expected to be removed from a bioelectrochemical system when the COD/N ratio is sufficiently low. Therefore, the MFC-PVDF/AC is used as a primary treatment to remove COD and a power source of MEC which is used in a downstream to remove ammonium nitrogen via the microbe-assisted anodic ammonium oxidation process. As a result, the MEC achieved an ammonium oxidation rate of and a nitrogen removal rate of  $0.173 \pm 0.01 \text{ kg NH}_4^+ \text{-N} / \text{m}^3/\text{d}$  and  $0.095 \pm 0.04 \text{ kg TN} / \text{m}^3 / \text{d}$  without aeration. This result suggests that ammonium nitrogen can be removed bioelectrochemically without aeration by an integrated MFC and MEC system.

In **Chapter 7**, the conclusions of individual chapters are summarized, and the outlook and remaining issues for a large-scale practical application of MFC technology are discussed. The present study demonstrates that the integration of MFC-PVDF/AC, LVBM and MEC is a promising approach to develop a cost-effective and energy-saving domestic wastewater treatment system with simultaneous renewable energy.



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This thesis is dedicated to all my family.

Thank God every 86,400 seconds!

# Chapter 1

## Introduction

### 1.1 General introduction of this study

The global population growth linked to rapid urbanization and rapid socio-economic development leads to the mass production of domestic and municipal wastewater effluents, which is one of the main ecological pollution issues. Currently, this constant rise in urbanization and intensive economic activities has forced urban areas to increase their wastewater treatment infrastructure to protect the public health and the environment. To date, the most successful and well-designed domestic wastewater treatment method for large-scale installations is the Conventional Activated Sludge (CAS) which is used to biologically and aerobically remove organic matter (as Chemical Oxygen Demand (COD)) and inorganic pollutant from domestic wastewater. The CAS is an energy-intensive technology and consumes an average of 0.45 kWh per m<sup>3</sup> of domestic wastewater (*ie* ~0.9 kWh per kg of COD removed), while half of this electric energy is used only for aeration process [1]. Furthermore, the CAS system used in traditional wastewater treatment plant releases a considerable amount of greenhouse gases into the atmosphere, such as nitrous oxide, carbon dioxide, and other volatile substances [2].

Nowadays, there is an increased understanding of the importance of sustainable wastewater treatment process. Wastewater is considered as a potentially valuable source of renewable clean energy. The most useful energy source stored in wastewater is the organic fraction

as measured by the COD [1] and capture this energy is of great significance for (i) meeting the world's energy needs, (ii) reducing wastewater handling costs and (iii) increasing the sustainability of wastewater treatment [2]. Theoretically, the potential energy in typical domestic wastewater has been estimated in the range of 4.1–4.9 kJ free energy/ kg COD, averaged at 4.5 kWh / kg COD (*ie* 2.3 kWh per m<sup>3</sup> of domestic wastewater) which is estimated to be about 5-fold the required electrical energy utilized to drive the domestic wastewater treatment via CAS process [1]. So, the major challenge is to efficiently capture the stored energy present in domestic wastewaters to meet the world energy demand and ensure a sustainable treatment process.

Microbial fuel cells (MFCs) has emerged as a promising technology due to its ability to employ electrogenic bacteria to simultaneously treat domestic wastewater and produce bioelectricity. MFC technology can convert the chemical energy stored in biodegradable substrates (COD) from wastewater into electric current using electrochemical active microorganisms (biocatalyst). In a MFC, electrogenic bacteria oxidize COD and release electrons to the anodic material which is used as a solid-state electron acceptor (anodic respiration process) while carbon dioxide (CO<sub>2</sub>) and protons (H<sup>+</sup>) are generated as a by-product. The electrons are spontaneously transferred through an external electrical circuit to the cathode where they are consumed in the reduction of oxygen. The MFC is considered as one of the most interesting low strength wastewater treatment systems because it could reduce the need of aeration due to the ability of electrogenic bacteria to oxidize COD by using anode material solid-state electron acceptor to breath (anodic respiration) rather than Oxygen. However, so far, the practical large-scale application of MFC technology is hindered first by using the cost-prohibitive material (platinum-catalyzed cathode for oxygen reduction reaction and Nafion<sup>®</sup> polymer separator and proton exchange membrane) and second by its poor performances in terms of effluent quality and low voltage output. Thus, to be

technically interesting, MFC should be less expensive, produce a good effluent quality and produce usable voltage output.

Recently, low-cost cathode material made by the fluorinated polymer (Poly(vinylidene fluoride, polytetrafluoroethylene ) using Activated Carbon (AC) as an Oxygen Reduction Reaction (ORR) catalysis has been successfully tested using synthetic wastewater [3–5]. However, the long-term performances of the MFC system (effluent quality, power output status of cathode) using real domestic wastewater as a substrate of MFC is missing. Also, to have a relevant acceptance as a sustainable energy source, MFC technology needs to generate useful output voltage ( $>3$  V). Due to its low working output voltage ( $<0.5$  V), MFC is often equipped with a Power Management System (PMS) to store the electrical energy from COD oxidation and boost the voltage to a valuable level.

To date, the commercially available or individually developed PMSs are not compatible with the MFC application and required a voltage  $>0.7$  V to function. Accordingly, the development of PMS suitable for MFC technology is required. So far, the limitations of MFCs technologies as an alternative large-scale domestic wastewater treatment and energy harvesting system are: (i) the use of cost-prohibitive the platinum-based cathode material (ii) the poor effluent quality (high COD and SS) which usually not compatible with the discharge requirement (iii) the low output voltage which is unusable, (iv) most the existing PMS are commercially available and are not suitable for the low voltage and low power output power source such as MFCs, (v) the poor performance in terms of nitrogen removal from domestic wastewater .

MEC is a recent anaerobic microbe-assisted electrolysis reactor that is commonly used to produce hydrogen gas ( $H_2$ ) during the COD oxidation by adding an external voltage ( $>0.2$  V) between the anode and the cathode [6]. Beside the microbial-dependent  $H_2$  production, a novel

application of MEC has emerged, namely microbe-assisted anodic  $\text{NH}_4^+$ -N oxidation without the need to supply  $\text{O}_2$  and  $\text{NO}_2^-$ -N, respectively. Thus, the association of MFC for COD removal and MEC for nitrogen removal for domestic wastewater application could offset the need for aeration.

## **1.1. Objectives of this study**

This study proposes a sustainable long-term domestic wastewater treatment and renewable energy harvesting by a MFC technology equipped with a newly developed low voltage booster multiplier. Furthermore, this study suggests to equip a MFC with a voltage booster for simultaneous COD removal and usable energy recovery and proposes a MEC for the treatment of ammonium-rich wastewater effluent from MFC reactor by the microbial-assisted anodic ammonium oxidation reaction.

The objectives of this study are as follows:

- Design a MFC reactor equipped with a low-cost AC catalyzed air-cathode for high COD and SS removal and good effluent quality over long-term operation.
- Develop a Low Voltage Booster Multiplier system which is a novel PMS compatible with the MFC technology to harvest valuable energy from COD oxidation.
- The use of MEC to treat anaerobically the ammonium-rich domestic wastewater via the microbe-assisted anodic ammonium oxidation process.

## **1.2. Outline of this dissertation**

This thesis consists of the following seven-part. **Chapter 1** provides the general introduction, objectives of this research and the outline of this dissertation.

**Chapter 2** provides literature reviews about MFC technology for sustainable domestic wastewater treatment. This chapter provides a description of the MFC principle and operating conditions. This part also provides the updated findings of MFC architecture and design for the domestic wastewater treatment. The comparison of the cost-effective anode material and carbon-catalyzed air-cathode are discussed in this section. This chapter also reviews the existing PMS technology used in the MFC field for sustainable energy harvesting application. The MEC principle, operating conditions, and current applications are also described in this chapter.

**Chapter 3** describes the design and the performances of the serpentine up-flow MFCs equipped with polyvinylidene fluoride (PVDF)-based activated carbon (AC) air-cathode (MFC-PVDF/ACs) and continuously operated for more than 6 months with real domestic wastewater as a substrate. The MFC-PVDF/ACs achieved average COD removal rates ( $5.11 \pm 0.94 \text{ kg-tCOD /m}^3/\text{d}$ ) and power densities ( $4.82 \pm 2.43 \text{ W m}^{-3}$ ) without major water leakage, which was comparable or even higher than those MFCs equipped with Pt-based air-cathode (MFC-Pts). The MFC-PVDF/ACs also achieved high and stable suspended solid (SS) removal efficiency ( $> 90\%$ ) at 1.5-h HRT without no clogging during the entire operation period. The PVDF-based AC air-cathode is much less expensive, more durable, and easy to manufacture, expensive Pt cathodes are not necessary for MFCs treating low strength domestic wastewater.

**Chapter 4** describes the design of the novel Low Voltage Booster system (LVB) which is developed specifically to boost the low voltage output of the MFC to the usable level. A LVB is used to increase the low output voltage of MFC-PVDF/ACs (i.e.,  $< 0.4 \text{ V}$ ) to a usable level ( $> 3 \text{ V}$ ). A single LVB was connected with a single MFC-PVDF/AC, which could increase the voltage from  $< 0.4 \text{ V}$  to  $4.35 - 5.2 \text{ V}$  without the voltage reversal, which was sufficient enough to turn on three LED bulbs for  $> 12$  days. Taken together, the MFC-PVDF/AC with a LVB circuit has an excellent

and stable performance of domestic wastewater treatment and power generation, suggesting that it could be used as a cost- and energy-saving primary wastewater treatment system, especially in developing countries.

**Chapter 5** describes the newly designed Low Voltage Booster Multiplier (LVBM) applied for the MFC technology. MFCs can produce renewable energy from wastewater, the output voltage and current are considerably low, which hampers the dissemination of MFC technology. Previously LVB was successfully designed to boost the low voltage from  $< 0.4$  V to 4.35 - 5.2 V without the voltage reversal, which was sufficient enough to turn on three LED bulbs for  $> 12$  days. To power an electronic device having higher nominal voltages  $> 24$  V, the serially stacked MFCs is often adopted but this approach leads to the voltage reversal issue.

To address this technical issue, we have newly developed a LVBM to boost and multiply the low output voltage from a single air-cathode MFC fed with domestic wastewater as substrate. The proposed LVBM is the final product of the LVB previously developed in chapter 4. The LVBM is a self-oscillating LVB coupled with a multistage voltage multiplier circuits (Cockcroft-Walton voltage multiplier circuit). The low output voltage (ca. 0.4 V) of MFC-PVDF/AC was successfully boosted up to  $89 \pm 22$  V (a maximum voltage of 127 V) without the voltage reversal and sustained at this level for several days by connecting a LVBM with 20-stage multiplier circuit. Moreover, a stable boosted voltage of  $52 \pm 0.8$  V was detected for more than 5 days even after disconnecting the LVBM from MFC-PVDF/AC (power source). The results suggest that the LVBM system is a suitable energy harvester and storage for a low power source such as MFCs. The proposed LVBM system is also inexpensive (¥ 1,000) and easy to set up. Therefore, it could be readily implemented in MFC technology.

**Chapter 6** describes the microbe-assisted anodic ammonium oxidation reaction in the and

nitrogen reduction MEC reactor. The bioelectrochemical anodic ammonium oxidation and nitrogen reduction of the MEC were investigated at various external voltages provided by a MFC and potentiostat. The MEC ammonium oxidation rate achieved  $0.173 \pm 0.01 \text{ kg NH}_4^+ \text{-N} / \text{m}^3 \text{/d}$  with a total nitrogen removal rate of  $0.095 \pm 0.04 \text{ kg TN} / \text{m}^3 \text{/d}$  at added voltage ca. 900 mV provided by a MFC ( $E_{\text{anode}}^0 = +525 \pm 264 \text{ mV}$ ). Similarly, adding 800 mV to the MEC electrical circuit via a potentiostat enables to achieve an ammonium oxidation rate achieved  $0.133 \pm 0.033 \text{ kg NH}_4^+ \text{-N} / \text{m}^3 \text{/d}$  and total nitrogen removal rate averaged at  $0.062 \pm 0.01 \text{ kg TN} / \text{m}^3 \text{/d}$  ( $E_{\text{anode}}^0 = +347 \pm 90 \text{ mV}$ ). This result indicated that the MFC could be used as a power source to remove treat nitrogen in wastewater. Moreover, ANAMMOX reaction was found to be the main route for nitrogen removal in the MEC fed and inoculated with domestic wastewater. This finding suggests that nitrogen could be removed bioelectrochemically first via microbe-assisted anodic ammonium oxidation, second, the produced  $\text{NO}_2^- \text{-N}$  from the anodic ammonium oxidation could be utilized by ANAMMOX bacteria for nitrogen removal.

**Chapter 7** provides a summary of the findings and recommendations for the large-scale application.



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## Chapter 2

### Literature reviews

#### 2.1 Microbial Fuel Cell technology

##### 2.1.1 Principle of Microbial Fuel Cell

Microbial Fuel Cell (MFC) is a sustainable bacteria-driven energy conversion device capable of converting directly chemical energy into electricity. MFCs employ microorganisms as biocatalysts to oxidize fuel and transfer electrons via substrate oxidation to the anode for bioelectricity production. Electrons and protons are released during the substrate oxidation. The produced electrons by electrochemically active bacteria are transferred to the anode usually under

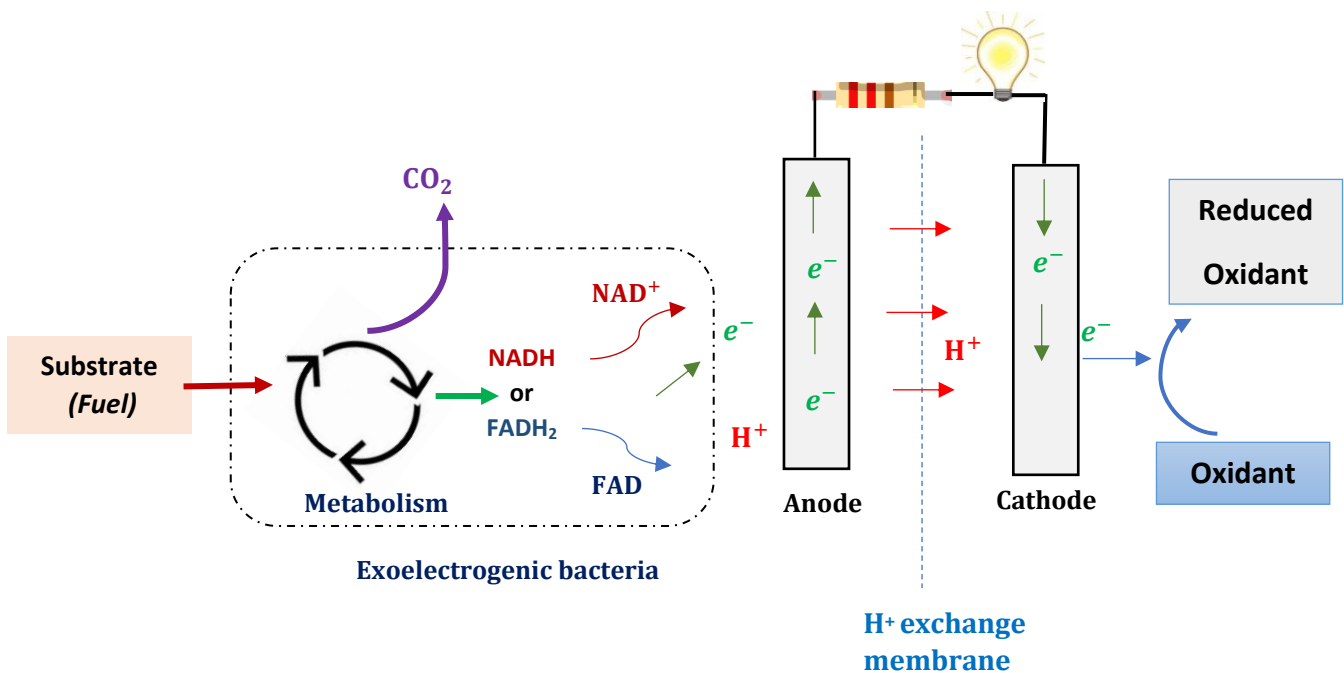


Fig .2. 1 : Principle of Microbial Fuel Cell

anoxic condition, then reach the cathode via an external electrical circuit. Protons are generated during the substrate oxidation and migrate from the anolyte through the proton diffusion layer to react with the electrons and oxidant to form a reduced by-product (**Fig 2.1**).

During the two decades, MFC has kept attention due to its ability to simultaneously treat domestic wastewater and harvest renewable energy. However, the large-scale application of MFC technology is not economically viable due to the use of expensive cathode (Platinum-based cathode) and separator material (Nafion<sup>®</sup>). Also, the poor performances in term of wastewater treatment and low voltage output are other limitations for its large-scale application.

### 2.1.2 Voltage output generated by a MFC

The electromotive force ( $E_{emf}$ ) of the overall reaction redox of the MFC is expressed as the potential difference between cathode and anode half-cell reaction as follow:

$$E_{emf} = E'_{cathode} - E'_{anode} \quad (1)$$

Where  $E'_{anode}$  and  $E'_{cathode}$  are the anode and the cathode potential, respectively and usually  $E'_{cathode} > E'_{anode}$  (Thermodynamically favorable overall reaction). The maximum  $E_{emf}$  (volt) attained by MFC if real domestic wastewater is used as an electron donor (fuel) and the oxygen as an electron acceptor is theoretically on the order of 1.14 V [ $+0.81V - (-0.33 V)$ ] (assuming wastewater as the electron donor and oxygen as the electron acceptor). However, when the electrodes are electrically connected via an external resistance, the measured MFC voltage ( $V_{MFC}$ ) drops due to several losses according to the equation (2). The Open Circuit Voltage (OCV) is expressed by equation (3).

$$V_{MFC} = E_{emf} - \eta_{anode} - \eta_{cathode} - I \times (R_{internal} + R_{external}) \quad (2)$$

$$\text{OCV} = E_{\text{emf}} - \eta_{\text{anode}} - \eta_{\text{cathode}} \quad (3)$$

Where  $\eta_{\text{anode}}$ ,  $\eta_{\text{cathode}}$  are overpotentials (potential losses) in the anode and the cathode,  $R_{\text{internal}}$ , is the internal resistance of the MFC and  $R_{\text{external}}$  is the applied external resistance and  $I$  is the bio-current generated by the MFC. In practice, OCV is in the range of 0.5–0.82 Volt due to the overpotentials. The overpotentials in a typical MFC is frequent due to the bacterial metabolic losses and the losses during the transfer of electrons from a compound reacting at the electrode surface [1]. The working output voltage of the MFC depends on the applied external load which is used to regulate the electron flow through the circuit. Usually  $V_{\text{MFC}}$  under Closed Circuit (CC) condition is <0.5 Volt.

### 2.1.3 Anode material for MFC technology

Anode material and structure affect bacterial biofilm attachment, electrons transfer, and, in some cases, direct substrate oxidation in a MFC reactor [2]. The exoelectrogenic transfer of electrons is conditioned by both the availability of the anodic electroactive surface area needed for electrogens to adhere and an efficient bacteria-anode electron transfer. This reason why a high-performance anode material enabling efficient EET is very important to enhance simultaneously the wastewater treatment efficiency and the power output of MFCs. Many different commercially available materials serving as an anode material has been documented so far. the commonly used anode materials are listed in table 2.1 However, a relevant anode material employed for MFC application need to fulfill some specific requirement to achieve an optimum anode-bacteria electron transfer.

A good anode material facilitates electron transfer donate by exoelectrogenic biofilm from bio-convertible substrate oxidation during the wastewater treatment process. The requirements of

an optimal anode material are: high electrocatalytic activity, highly electron-conductive, non-corrosive, high specific surface area (area per volume), high porosity, high biocompatibility, non-fouling (i.e. the bacteria do not fill it up), chemically stable, long-term stability, eco-friendly material, inexpensive, easy to manufacture and scalable for larger application [3,4]. Also, high roughness for accommodating a large number of microbes, and efficient electron transfer between bacteria and the electrode surface, are essential for high bio-electrocatalytic activity [5]. Furthermore, the anode material should be electrochemically and bioelectrochemically inert and non-active for a large variety of chemical and biocatalyst compound in the anolyte under a wide range of anolyte potential (-400mV; +820 mV vs SHE). Taking account of the probable industrial-scale production plant, the manufacturing process of this hypothetical anode should be more affordable and environment-friendly as possible. the commonly used anode material and their properties are listed and discussed in table 2.1

### **2.1.3.1 Carbon-based anode materials**

For a large-scale application, the anode material should be abundant and easy to manufacture without any environmental drawback. Because the electron transfer from exoelectrogenic biofilm to bacteria is a surface-based reaction rather than volume base reaction in suspension fermentation, a large overall anodic surface is required to carry out the organic matter oxidation for higher power output [2]. The most commonly used anodes are carbon-based fabrics, such as carbon cloth [6], carbon paper [7], carbon mesh [8], carbon felt or foam [3], activated carbon felt [9], graphite carbon granules [10], graphite foam[11], graphite felt [12], graphite rod [13], graphite plate [14], Reticulated Vitreous Carbon (RVC) [15] and Carbon fiber brush [16].

The advantages of these materials are their high electric conductivity, good microbial compatibility and large surface area. Generally, material structures with a higher specific surface

area are expected to provide more colonized sites for bacteria, resulting in higher power output. However, one should note that only those surfaces accessible to bacteria are responsible for the current generation; those pores with a diameter less than 2 nm, for example, are too small for bacteria to access, thus are not beneficial to electricity production [3].

*Carbon fiber- paper- foam –cloth.* Carbon fiber, paper, foam, and cloth (Toray) have been extensively used as electrodes [17] with the unique advantage of reduced electrode spacing due to their planar geometry, leading to reduced internal resistance and higher volumetric power density [4]. Carbon cloth is more flexible and appears to have greater porosity than carbon paper, whereas carbon foams are much thicker than the cloths, conferring more space for bacterial growth [3].

*Graphite rods, felt, foams,* Current generated by MFCs equipped with a graphite rod, graphite felt and graphite foam were compared in 2003 [11]. These results indicated that the current density of graphite felt and graphite rod exhibit respectively comparable to 28 mA /m<sup>2</sup> and 31 mA/m<sup>2</sup>. But it has been observed that the graphite foam produced the greatest power density of 74 mA/m<sup>2</sup> and is attributed to more cells attaching to the foam because of its structure [18].

*Carbon Fiber Brush.* For unmodified carbon-based anodes, electrocatalytic efficiency depends on the oxidation of microorganisms on the anode. Increasing the anodic surface area is an efficient and widely utilized approach, and various strategies have been used to make carbon materials with a large electrochemically active surface area [19]. The Carbon fiber brush is a three-dimensional structured electrode for MFCs developed by Logan et al. in 2007 [20]. This brush anode is made of bristled carbon fibers stowed onto a twisted non-corrosive metal, such as the titanium wire [3]. The fine diameter of fibers (7.2 μm) combined with their densely bundled arrangement (about 400,000 tips per inch) conferring an extremely high surface area [3,21]. Its

Carbon-based porous structure network and large surface area provide the microorganism with easy access onto the anode surface. The brush anode has the largest surface area and a highly porous structure of all carbonaceous based anode material documented so far [19] that permit to increase the loading amount of bacteria and thus enhance its electrocatalytic performance. For example, it has been reported the cube single chamber MFC with a brush anode achieved a maximum power density of  $2400 \text{ mW/m}^2$  or  $73 \text{ W/m}^3$ , which is more than double that of the same MFC with carbon cloth anode [22]. Carbon fiber brush anodes can be used in MFCs to achieve good rates of COD removal, they have high surface areas and porosities for growth of exoelectrogenic microorganisms, and they produce stable power over time using actual domestic wastewaters [23].

So far, the Carbon fiber brush is considered to be an ideal anode material and with high surface area, high porosities, and efficient current collection [24]. Unlike other high specific surface area materials, such as carbon foams, which could become filled with bacteria and be difficult to unclog, current generation was not adversely affected by biofilm growth on the brush anode surface, and system performance improved over time with biofilm development [22]. The success of carbon fiber brush could be explained because it was designed exclusively as an anode material for the MFC, whereas the other commercially available materials were not specifically designed for this purpose. Another asset of the carbon fiber brush is the easiest way to connect electrically the non-corrosive and already existing titanium core serving as a current collector compared to others anode material such as carbon mesh, carbon foam or granular activated which need to be carefully connected to and exogenous current collector.

**Table 2. 1:** Comparison of anode material properties frequently used in an MFC technology.

Unmodified Anode Materials	Surface area	Conductivity	Scalability condition	MFC efficiency	advantages	Technical Limitations
<b>Activated carbon cloth (C-tex®)</b>	700 to1200 m <sup>2</sup> g <sup>-1</sup> [25]	1 to 8 Ω sq <sup>-1</sup> [26]	Affordable, readily scalable, environmental issue	482 A/m <sup>3</sup> [25]	Excellent conductivity, Highly porous, higher adsorption capacity compared to GAC High surface area available for MET	Thin material easy to deform
<b>Activated carbon nanofiber nonwoven ACNFN</b>	1158.75 m <sup>2</sup> g <sup>-1</sup> [27]	0.19 S/cm [27]	Affordable, readily, environmental issue	2715 A/m <sup>3</sup> 758 W/m <sup>3</sup> ; [27]	Simple manufacture process nano-sized features and a macroporous structure into one material. high porosity (70%) [27]	Electrical connection issue
<b>Activated carbon felt</b>	900 to 2500 m <sup>2</sup> g <sup>-1</sup> [9]	NA	Affordable, readily scalable, environmental issue	1304 mW/m <sup>2</sup>	Good biocompatibility and low-cost material, very high surface area that can help the adsorption ability.	Electrical connection issue
<b>Granular activated carbon (GAC)</b>	842.63 m <sup>2</sup> g <sup>-1</sup> [27]	NA	Affordable, readily scalable, Easy to manufacture, environmental issue	161 W/m <sup>3</sup> ; [27]	Good biocompatibility and low-cost material, very high surface area that can help the adsorption of organics pollutants or heavy metals [28]	Lower electrical conductivity usually used as packed material, risk of clogging
<b>Carbon paper (CFP)</b>	10 m <sup>2</sup> g <sup>-1</sup> ,	0.5 Ohm sq <sup>-1</sup> [29] 0.8 Ω cm <sup>-1</sup>	Not technically viable for MFC	327 A/m <sup>3</sup> [25]	Easy to connect wiring [3]	Lack of durability, Brittle [3], Expensive \$1,000/m <sup>2</sup> [30]
<b>Carbon cloth</b>	31.3 m <sup>2</sup> g <sup>-1</sup> [31]	2.2 Ω cm <sup>-1</sup> [3]	Difficult to scale up [20]due to higher electrical resistance [32]	3.4 W/m <sup>3</sup> [27]	Flexible, large porosity [3]	Thin, expensive [20] \$1,000/m <sup>2</sup> [33],mechanical fragile [34]
<b>Carbon felt</b>	35.3 m <sup>2</sup> g <sup>-1</sup> [31]	280 S/cm [35]	Not technically viable for MFC	77.82 mW/m <sup>2</sup> [36]	Large porosity, high surface area [37] , Mechanical stability ,less expensive \$10–50/m <sup>2</sup> [33]	highly hydrophobic [37]
<b>Carbon foam</b>	30.0 m <sup>2</sup> g <sup>-1</sup> [31]	NA	Difficult to scale up [20]	NA	Thicker conferring large space for bacterial growth [3]	Electrical connection issue
<b>Carbon mesh</b>	NA	NA	Affordable, readily scalable, Easy to manufacture	NA	Relatively cheap (10-40 us dollar/m <sup>2</sup> ) [32], large porosity	Thin, easy to deform
<b>Graphite rod</b>	~10 m <sup>2</sup> g <sup>-1</sup> [38]	0.2 Ω cm <sup>-1</sup> [3]	Affordable, readily scalable, Easy to manufacture	NA	Good electrical conductivity and chemical stability, relatively cheap, and easy to obtain	Low surface area, low internal porosity [3]
<b>Graphite felt</b>	0.7 to 2000 m <sup>2</sup> g <sup>-1</sup> [39]	NA	Affordable, readily scalable, Easy to manufacture	175.7 mW/m <sup>2</sup>	Large porosity, good conductivity and stability	High cost
<b>Graphite foam</b>	NA	NA	Difficult to scale up [20]	NA	Largest surface area, higher porosity, easy to produce	Electrical connection issue
<b>Graphite fiber brush</b>	7 170 m <sup>2</sup> /m <sup>3</sup> -brush volume [3]	1.6 Ω /cm	Readily scalable [20]	2400 mW /m <sup>2</sup> [22]	Largest surface area , higher porosity [19] easy to produce [3]	Clogging by particulate material
<b>Granular Activated carbon granule</b>	820 to 2700 m <sup>2</sup> m <sup>-3</sup> [3]	0.5-1.0 Ω /granule [3]	Difficult to scale up [20], technically not viable.	1.2 W/m <sup>3</sup> [40]	Good adsorption ability biocompatible, inexpensive, long durability	Electrical connection issue, high ohmic resistance,
<b>Reticulated Vitreous Carbon</b>	6500 m <sup>2</sup> m <sup>-3</sup> [41]	200 S cm <sup>-1</sup> (5x10 <sup>-3</sup> Ω cm). [3]	Readily scalable but technically not viable	NA	Excellent electronic conductivity, porous material [3] , higher surface area, low resistance to fluid flow [42].	Brittle material [3] poor bacterial adhesion due to vitreous and smooth surface area , very small pore size for bacterial penetration [43]



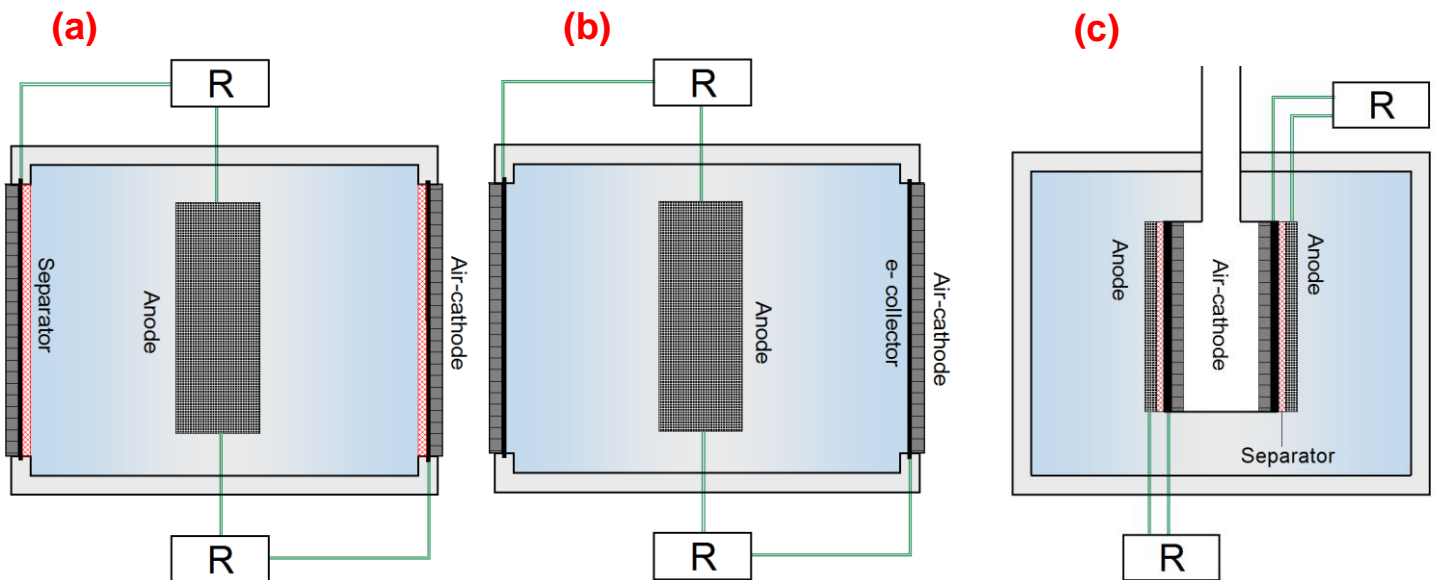
Unmodified Anode Materials	Surface area	Conductivity	Scalability condition	MFC efficiency	advantages	Technical Limitations
<b>Carbon Nanotube fiber (CNF)</b>	100-600 m <sup>2</sup> g <sup>-1</sup> [44]	8.3 x10 <sup>7</sup> S cm <sup>-1</sup> [45]	Hinder by health and environmental risk [46]	172 mW /m <sup>2</sup> [47]	Excellent electronic conductivity, large surface area, nanostructuring promotes excellent bacterial growth and adhesion.	Toxic for bacteria, very expensive (\$780/5g) [48]
<b>Graphene sheet</b>	2630 m <sup>2</sup> g <sup>-1</sup> [5,49]	~2 S cm <sup>-1</sup> [49]	Readily scalable, not economically viable		High conductivity and surface area [5].	High hydrophobicity poor biocompatibility [50]. Complicated synthesis increasing capital cost in large-scale applications [51] .
<b>Graphene oxide nanoribbon</b>	38 m <sup>2</sup> g <sup>-1</sup> [52]	NA	Readily scalable, not economically viable	34.2 mW /m <sup>2</sup> [53]	Higher surface area for bacterial adhesion	Possible anti-bacterial effect
<b>3D Graphene foam</b>	~850 m <sup>2</sup> g <sup>-1</sup> [54]	~ 10 S cm <sup>-1</sup> [54]	Readily scalable, not economically viable	12.8 mW /m <sup>2</sup> [50]	High porosity and surface area , larger pore size for internal bacterial diffusion [50].	High hydrophobicity poor biocompatibility [50]. Complicated synthesis increasing capital cost in large-scale applications [51] .
<b>Reduced graphene sheet</b>	NA	NA	Readily scalable, not economically viable		Good bacterial adhesion and high conductivity	Possible anti-bacterial effect
<b>Stainless steel grade 304</b>	NA	1.450x10 <sup>8</sup> S cm <sup>-1</sup> [55]	Relatively cheaper, easy accessibility		Good mechanical properties, High electrical conductivity, can be mass-produced, durable, relatively inexpensive	Non-porous material, Smooth surface, poor biocompatibility [3], corrosion may occur due to residual O <sub>2</sub> [34].
<b>Titanium</b>	NA	1.798 x 10 <sup>8</sup> S cm <sup>-1</sup> [55]	Affordable, readily scalable, Easy to manufacture		Good electrical conductivity can be mass-produced, durable, relatively inexpensive	Non-porous material, Smooth surface, poor biocompatibility [3]
<b>Pure Copper</b>	NA	6.009 x 10 <sup>9</sup> S cm <sup>-1</sup> [55]	Readily scalable but Technically not viable		Good electrical conductivity can be mass-produced, durable, relatively inexpensive	Non-porous, readily corrosive material, highly toxic for bacterial, poor biocompatibility, communities, unsuitable for MFC work [3], [56]

### 2.1.4 MFC architecture

The configuration of MFC is quite various including a two-chamber MFC and a single chamber air-cathode MFC. A double-chambered MFC has also been designed to drive abiotic cathodic reduction reaction in a catholyte such as a ferricyanide, permanganate, hydrogen peroxide. Ferricyanide and permanganate were often used as a catholyte in the lab-scale [33], but the use of these chemicals in the cathodic solution is not sustainable and would therefore not suitable for large-scale systems [20]. The aerobic biocathode in a MFC technology use aerobes as a catalyst and achieved the reduction of oxygen [57]. However, the drawback of this aerated

catholyte solution is the intensive aeration which is uneconomical. However, the catholyte aeration could be practically avoided by adopting a single chamber air-cathode MFC design.

The large application MFC-based municipal wastewater treatment requires cost-effective material and configuration and eco-friendly oxidant as possible. Also, the design must be simple, less space-consuming and easy to scale up. The one-compartment air-cathode MFC was designed to eliminate the need for an aerated cathode, the use of expensive and harmful oxidizing agent such as ferricyanide, permanganate, and other harmful and expensive oxidant. Accordingly, the single chamber MFC architecture is less expensive and more practical than the conventional two-compartment system, which requires aeration and the need to build an extra cathode chamber.



**Fig .2. 2 :** Air-cathode MFC architecture:(a) a single chamber MFC with Separator Electrode Assembly; (b) Separator-less single chamber MFC (without Proton Exchange Membrane); (c) Submerged air-cathode MFC with sandwich-type Separator Electrode Assembly.

In a single chamber design, the air-cathode design is very interesting because oxygen from ambient air is freely used as an oxidant and reduced by-product is water molecule. The single chamber air-cathode architecture is a response to fulfill the requirement of sustainability, economical architecture, and scalability in the MFC field. The first air-cathode MFC was reported by Sell et al. in 1989, but this study was unknown to many MFC researchers as this paper was not cited in early air-cathode studies [3]. The application of single chamber air-cathode MFCs was successfully applied for domestic wastewater treatment by Liu and Logan in 2004 [58]. The single chamber air-cathode MFC design offers the possibility to use our immediate environment as a cathodic chamber. On a large-scale, this configuration can considerably reduce the space occupied by the bioreactor in case of large-scale application, making MFC technology more compact thus interesting for the urbanized area for instance.

A single chamber air-cathode MFC can be divided into three possible architecture: The single chamber air-cathode with or without electrode separator assembly and the submerged air-cathode chamber configuration (**Fig 2.2**). Furthermore, these air-cathode MFC configurations allow the reduction of the anode-cathode distance, increasing the Proton transfer efficiency [4,59]. The separator has a role to isolate the anode to the cathode in two distinct compartments. Also, it allows the transfer of protons from anode to cathode, avoid electrical short circuit and prevents oxygen crossover into the anolyte solution. A Proton Exchange Membrane (PEM) such as Nafion<sup>®</sup> is the most frequently used separator in MFCs due to its moderately high cationic conductivity and low internal resistance compared to other separators [60]. However, its application at large-scale in the field of MFCs is uneconomical (\$700/m<sup>2</sup>) [60]. It has been reported that separator-less single chamber air-cathode MFC (**Fig 2.2b**) as the most effective MFC design for wastewater treatment

even if some higher power output can be achieved by adding PEM at the cathode (**Fig 2.2a and 2.2c**) [61].

### **2.1.5 Recent platinum-free and low-cost air-cathode for MFC application**

Oxygen present in the ambient air offers an exergonic redox reaction permitting electrons to flow from anode to cathode [62]. Oxygen is an ideal electron acceptor for MFCs because of its high redox potential, availability and sustainability [63]. Usually, the oxygen reduction reaction rate is kinetically sluggish, resulting in a large proportion of potential loss [62,63]. Most of commercially available air-cathode for the fuel cell technologies was made by a Nafion<sup>®</sup> as a binder and diffusion layer with noble-metal as an oxygen reduction catalyst, are both cost-prohibitive material. Platinum (Pt)-based catalysts are widely used as the air-cathode MFC material to speed up oxygen reduction rate (ORR) [64]. Although platinum shows a high ORR, the large application as an air-cathode MFC-based catalyst is limited because of its rare and cost-prohibitive material even at lab-scale, therefore, not economically interesting at large-scale [62].

Air-cathode materials need to be durable and inexpensive, and the fabrication should require relatively simple procedures, time-saving process, less labor-consuming process and also the use of inexpensive or low energy consumption equipment [65]. More recently many types of research have been led to find a non-cost prohibitive air-cathode based on the non-precious metal carbon-based catalyst. Interestingly, Activated Carbon (AC) was found is an inexpensive and sustainable catalyst for oxygen reduction in air-cathodes MFCs [66]. This finding of low-cost carbon-based ORR catalyst opened the way to implement MFCs technology as valuable municipal wastewater treatment unit at a larger scale.

Dong and coworkers early proposed to employ polytetrafluoroethylene (PTFE) as a binder to replace the expensive Nafion® with AC as a low-cost ORR catalyst via the rolling press method [67]. In this study, the PTFE-based air-cathode achieved a maximum power and current densities of 802 mW/m<sup>2</sup> and 3.4 A/m<sup>2</sup>, respectively. Unfortunately, this Pt-free PTFE-based air-cathode fabrication is relatively complicated because its fabrication requires two distinct steps to fabricate the Gas Diffusion Layer (GDL) and the Catalyst Layer (CL) and requires extra heating energy of 340 °C to be dry prior to use (**table 2.2**).

Poly(vinylidene fluoride) (PVDF) was reported to be also advantageous over other membrane materials due to its high mechanical strength and excellent chemical resistance, in which these properties make it suitable for wastewater treatment [68]. In 2014, Zhang developed a simple one-step, phase inversion process to construct an inexpensive MFC cathode using a PVDF binder and AC as an ORR catalyst. In this study, the PVDF-based air-cathode achieved a good power performance (1470 mW/m<sup>2</sup>). Furthermore, this low-cost air-cathode material was able to withstand a pressure of 1.2 meter. From a cost perspective of the platinum-free air-cathode fabrication applied for large-scale MFC, PVDF-based air-cathode is the best candidate.

**Table 2. 2** Comparison of fabrication procedure of the recent platinum-free PTFE-based air-cathode and PVDF-based air-cathode using activated carbon as an Oxygen Reduction Reaction Catalyst. GDL: Gas Diffusion Layer, CL: Catalyst Layer.

Air-cathode for MFC	Descriptions of the fabrication	MFC efficiencies	Ref.
PTFE-based air-cathode	<p><b>Advantages:</b> Pt-free, good chemical and pressure resistance (3 m of water [69]) . low-cost material (25 \$/m<sup>2</sup>).</p> <p><b>Limitations:</b> Relatively complicated process and require two-step fabrication of GDL and CL. But requires long fabrication process. and require extra heating energy at 340 °C for 2 hours for the drying process.</p>	802 mW/m <sup>2</sup> (3.4 A/m <sup>2</sup> )	[67]
PVDF-based air-cathode	<p><b>Advantages:</b> Pt-free, single-step phase inversion for the fabrication of GDL and CL. Very simple and time-saving Fabrication at room temperature (no need of heat treatment) can resist up to 1.2 m of water, low-cost material (15 \$/m<sup>2</sup>). Fabrication process duration around 15 minutes</p> <p><b>Limitations</b> Drying process at room temperature requires 8hours.</p>	1470 mW/m <sup>2</sup>	[68]

## 2.2 Power Management System (PMS) to harvest renewable energy from MFC as a power source.

The MFC is a green technology which offers an opportunity to generate renewable electrical energy source from bacterial EET reaction during the wastewater treatment process. The low voltage level of the MFC is one of the limitations of the MFC as a sustainable power source compared to an existing green power source such as thermoelectric generator (4 V) and solar panel (12V). The working voltage of a typical single MFC unit is less than 0.5 V which is too low to drive a small electronic device such a Light Emitting Diode (LED) or microsensors which have a nominal voltage of 2.5 V. To increase the output voltage to a usable level, MFCs are often

associated in series, to sum up the individual working voltage. However, the serially stacked MFCs involve the voltage reversal due to inversion of the polarity of the electrodes when the fuel (substrate) shortage occurs. As a result, the stacked voltage becomes low compared to the sum of the individual MFC's output voltage [70–72]. To harvest valuable renewable energy from MFC, a PMS is often used instead of the traditional external resistance [71,73,74]. A PMS consist of electronic components such as boost converters, charge pumps, rectifiers, regulators, and capacitors, performs the function of (i) harvesting energy from usable energy sources (ii) and boosting the low voltage source into a usable level [71]. Unfortunately, the commercially available PMSs system used in the most MFC studies were not designed specifically for the low voltage and low current source such as (working voltage <0.5 V, Bacterial EET current ranged from 1 mA-12 mA). To date, the individually developed PMS for MFC application use the electronic components requiring an input voltage beyond the working voltage of the single MFC. Accordingly, in most cases, the need of serially stacked MFCs is needed, but this approach leads to a voltage reversal issue. Therefore, developing a PMS designed specifically for MFC technology as a sustainable power source is crucial for real-world application. Accordingly, a customized voltage booster compatible with the low voltage output of MFC for the more practical range of voltage application (> 3V) needs to be developed.

### **2.3 Air-cathode MFC for domestic wastewater treatment**

The application of MFC for domestic wastewater treatment has been widely investigated during the last decade. Organic matter (COD) from domestic wastewater could be oxidized by exoelectrogenic bacteria under anaerobic condition using anode as an electron acceptor (termed as anodic respiration). Table 2.3 presents some application of MFC for wastewater treatment.

However, the COD removal efficiency in a MFC reactor depends on the several factors including electrodes material, the hydraulic retention time (HRT), the reactor configuration, and the electrical connection. A MFC having a multiple anodes and cathodes configuration was found to be suitable for domestic wastewater treatment. The increase of HRT is an effective method to enhance wastewater treatment of MFC [75]. For example, Seon and coworkers reported that the COD removal increased from 66 to 88% when the HRT increase from 6 to 8 hours [76]. Among the existing reactor configuration, up-flow MFC treating domestic wastewater was found to achieve high COD removal efficiency (89%) at relatively short HRT (see table 03). The COD removal in a MFC also depends on the electrical condition and the external resistance. It was observed that the closed circuit condition accelerate the COD removal in a MFC fed with domestic wastewater under ( $R_{ext} = 100 \Omega$ , COD removal ca.85%) which was 10-fold higher than the open circuit condition (no current) [77].



**Table 2. 3** : Performance of air cathode MFCs treating domestic wastewater

MFC type	working volume (L)	HRT (h)	R ( $\Omega$ )	COD <sub>in</sub> (mg/L)	COD <sub>out</sub> (mg/L)	COD <sub>rem</sub> (%)	COD RR (kg-tCOD/m <sup>3</sup> /d)	CE (%)	I <sub>D mean</sub> (A/m <sup>3</sup> )	P <sub>D mean</sub> (W/m <sup>3</sup> )	Ref.
Plug flow MFC (stack)	250	144	1	333.33	70±17	79	0.04	3~5%	1.74	0.47	[78]
Pilot-scale MFC	44.8	22	75	118	90	24	0.031	24.8	na	0.220	[79]
MAC-MFCs	20	5 ~20	100	100~1000	30~80	66 - 88	0.4 ~0.55	0.3	na.	0.16 ~ 0.2	[80]
SEA-MFC	6.1	4	20	~500	100-200	57 ± 15	1.71	28	na.	6.0 ± 0.4	[81]
air-cathode MFC	0.14	4.4	200	~400	>100	48.3	na	18~29	na	12.3	[82]
air-cathode MFC	0.028	0.22	500	500	371	25.8	13.93	1.7	~50	12.8	[83]
SEA-MFC	0.15	0.5	50	144 ± 18	~60	34 ± 5 (max =42)	2.90	na.	60 ± 33	12.9 ± 2.9	[84]
SEA-MFC	5.7	6 ~ 8	50	108	20~35	66-80	0.23 ~ 0.344	< 6	na	0.350 ~0.534	[76]
SEA-MFC	0.1	2	100	~400	218	~45.5	2.18	45.1 ±1.0%	na	18.84	[85]
MFC (stack)	0.028	0.33	na	340~446	~200.5	44	11.3	1.8~13	28.3	12.8	[86]
ABMFC	1.6	192~288	1000	237.78 ± 7.65	44.16 ± 1.91	80.21	na	17.01	na	0.01	[87]
UBEF	0.184	5.52~6.72	1000	120~450	na	89	na	0.25~1.51	0.31±0.02	0.103	[88]

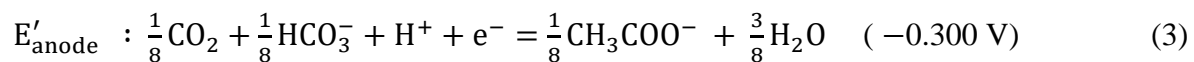
SEA-MFC: Separator electrode assembly MFC, MAC-MFC: multi-anode/cathode microbial fuel cells, ABMFC: algae biofilm microbial fuel cell, UBEF: up-flow bioelectrochemical filter, na.: not available, P<sub>D</sub>: power density, I<sub>D mean</sub>: mean current density, CE: Coulombic efficiency, COD RR: COD removal rate, R : applied external resistance ( $\Omega$ ) .

## 2.4 Microbial Electrolysis Cell technology (MEC) principle and application

The Microbial Electrolysis Cell (MEC) is a microbe-assisted anaerobic electrolysis reactor used to treat (oxidize) organic and inorganic pollutant present in wastewater. MFC and MEC technologies utilize the same electrode materials such as cloth carbon paper, graphite felt, graphite foam, graphite fiber brushes and metallic electrode material such as nickel foam and stainless steel mesh. The MEC consist of anode, cathode, external power source and electrochemically active microbial communities mainly applied for wastewater treatment and biogas (H<sub>2</sub> or CH<sub>4</sub>) recovery. In the MEC system, the anode and cathode materials are determined by the electrical connection to the power source (the anode and cathode connected to the positive and negative terminal of the external DC power source, respectively) (**Fig 2.3**).

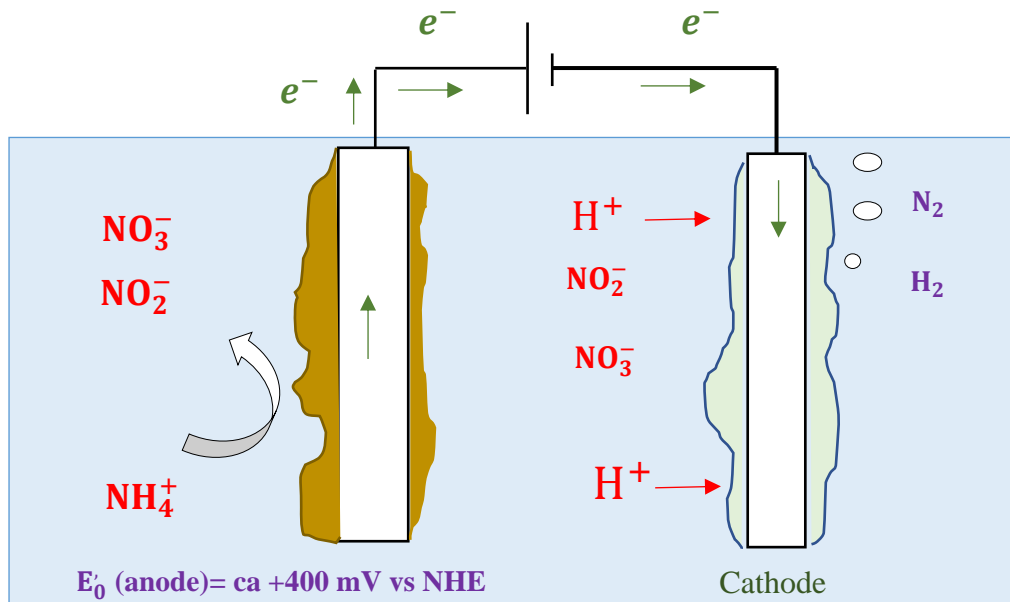
In a MEC, exoelectrogenic bacteria colonize the anode and oxidized organic or inorganic substrate releasing proton and electrons. The *exoelectrogens* transfer the electrons to the anode material (anodic respiration) while protons are released in the electrolyte (bulk solution). MEC was widely investigated for hydrogen or methane production using various substrates such as glucose, acetate or real domestic wastewater.

If the MEC is used for hydrogen production with acetate as a carbon source, the cell voltage is given by the equations below:



$$E'_{\text{cell}} = E'_{\text{cathode}} - E'_{\text{anode}} = (-0.414 \text{ V}) - (-0.300 \text{ V}) = (-0.114 \text{ V}) \quad (5)$$

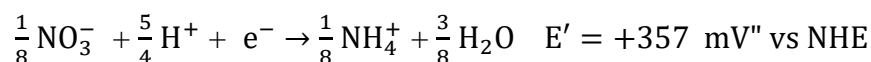
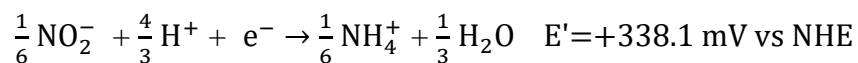
The negative value of the equation (5) indicates that the hydrogen production reaction using MEC has a deficiency of cell voltage of 0.114 V (not spontaneous reaction). Accordingly, the MEC needs a minimum theoretical applied voltage of 0.114 V from a DC power source to produce H<sub>2</sub> gas. In practice, an applied voltage ranging from 0.2 V to 0.8 V is required to offset the potential losses (overpotential) during the wastewater treatment process. the MEC could be powered by a DC voltage source such as a potentiostat or by a typical MFC having a working voltage >0.2 V.



**Fig .2. 3 :** Electricity-assisted anodic ammonium oxidation in a MEC: ammonium oxidation at the electropositive poised anode coupled by the cathodic dependent nitrogen reduction.

The MEC was successfully applied for COD removal from wastewater influent and biogas production. The oxidation of ammonium in wastewater is traditionally associated to a biological process performed using various acceptors such as oxygen (aerobic process), Nitrite (ANAMMOX process) or iron -III (Feammox process). Ammonium removal in a typical MFC has already observed and more often attributed to aerobic nitrification due to the passive intrusion of oxygen into the reactor. Furthermore, autotrophic anodic ammonium oxidation catalyzed by *Nitrosomonas europaea* with an anode as the electron acceptor has been documented [89,90]. Later, Zhang and

coworkers reported an autotrophic ammonia oxidation to nitrogen gas using microbes as biocatalyst on the anode, with a polarized electrode (+600 mV vs. Ag/AgCl) as electron acceptor [91]. More recently in 2018, the microbial-assisted anodic ammonium oxidation was confirmed using a MEC reactor published identifying *Brocadia* genera, *Kuenenia* (ANAMMOX), *Nitrospira* and *Nitrosomonas* (AOB) genera in the anodic biofilm [92]. These findings suggest that under autotrophic condition, ammonium could be oxidized via anodic respiration route process using some nitrifying bacteria genera as a biocatalyst. The bioelectrochemical anodic ammonium oxidation process which is electrochemically poised at the oxidative ammonium oxidation potential value according to the following equations:



In other words, anodic material could alternatively play the role of solid electron and acceptor for ammonium oxidation near-zero presence of well-known dissolved (or insoluble) electron acceptors when the anodic potential value is more electropositive (ca.+400 mV vs. NHE) described in Figure 2.3. Thus, the positive value of the anode could mimic the potential of traditional dissolved electron acceptor usually found in the natural environment.

## Conclusion

The MFC an interesting technology due to its dual ability to treat wastewater and generated directly bioelectricity. The large-scale was impeding mainly by the cost of the electrode material which is made by cost-prohibitive material such as Nafion<sup>®</sup> and the Platinum catalyst. To date, some recent improvement offers the new opportunities to engineer a novel, scalable and cost-

effective Activated carbon-catalyzed cathode for the MFC application. The PVDF-based air-cathode is a promising material which was successfully tested with the MFC fed with for synthetic wastewater treatment. The MFC equipped with the PVDF-based air-cathode exhibited good power performance and was reported to be strong enough to withstand a water pressure of 1.2 m [68]. Therefore, the durability of the PVDF-based air-cathode material applied for the MFC treating real domestic wastewater needs to be investigated over a long period of time and the performances in terms of efficiencies and power output need to be compared with those MFCs equipped with a commercially available platinum-catalyzed air-cathode MFC. A customized PMS needs compatible with the low voltage MFC. Accordingly, a PMS for MFC technology need to be developed to harvest valuable energy from wastewater treatment. The anodic ammonium oxidation could be a sustainable strategy to treat ammonium-rich wastewater via MEC (needless aeration). Thus, the integrated MFC-MEC technology for both COD and ammonium removal could reduce the cost of real domestic wastewater treatment.

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## **Chapter 3**

# **Domestic wastewater treatment by serpentine up-flow MFCs equipped with PVDF-based activated carbon air-cathodes**

### **3.1 Introduction**

Microbial fuel cells (MFCs) have been considered to be a potential energy-saving or recovering wastewater treatment process [1–3]. A great variety of studies have been conducted extensively for last two decades. However, practical application of MFCs to domestic wastewater treatment is still challenging due to insufficient treatment performance (i.e., COD and SS removal), low power output (i.e., energy recovery), high capital cost, and lack of scalability. In MFCs, COD is oxidized by exoelectrogens without aeration (that is anodic respiration), which results in insufficient effluent water quality despite reducing energy demand for aeration [2,4]. Requirement of post-treatment offsets the benefits of MFCs for practical application. Domestic wastewater is characterized by low solution conductivity and biodegradable COD concentration [5], resulting in low power generation [6]. The generated voltage is too low to be used directly for many practical applications, which has been a large obstacle in energy recovery by MFCs [7]. To avoid high energy demanding aeration of the typical domestic wastewater treatment process, air-cathode MFCs are considered to be more suitable for wastewater treatment since oxygen has become the most common terminal electron acceptor in the cathode [8]. Precious and expensive metals such as platinum (Pt) is usually used for cathode catalysts because it has high oxygen reduction reaction

activity [9]. However, platinum is too expensive to be used for large-scale wastewater treatment plants in practice [10,11]. In addition, air-cathodes must be watertight and durable, showing high water pressure resistance, even in large-scale MFCs. Recently, a relatively large window-pane cathode ( $0.62 \text{ m}^2$ ) and water pressure resistant ( $0.85 \text{ m}$  water height) was successfully installed in  $85 \text{ L}$  MFC, which generated a power density of  $0.083 \pm 0.006 \text{ W m}^{-2}$  using wastewater as a fuel [12]. For practical application to domestic wastewater treatment, MFCs should be inexpensive, scalable, and watertight (withstand high water pressure) and produce good effluent water quality (meet effluent standard so that no need of post-treatment) and usable power.

The objective of this study is therefore to develop such desirable MFCs for domestic wastewater treatment having a good effluent quality and usable power output. In addition, the generated power must be boosted up to usable levels. In this study, we manufactured serpentine up-flow MFCs equipped with polyvinylidene fluoride (PVDF)-based activated carbon (AC) air-cathode (MFC-PVDF/AC) and graphite carbon brush anodes. To our knowledge, there have been only a few studies on real domestic wastewater treatment by PVDF-based air-cathode MFCs. Yang et al., (2014) fabricated PVDF-based activated carbon (AC) air-cathodes and tested their durability and power output using domestic wastewater as substrate but have not evaluated its wastewater treatment performance. Similarly, polytetrafluoroethylene (PTFE)-based AC air-cathodes were fabricated and tested for power generation [12–16]. However, the long-term treatment efficiencies of real domestic wastewater were not evaluated in these studies, which is essential to assess the practical application. Therefore, we have continuously operated MFC-PVDF/ACs with real domestic wastewater for more than 6 months, evaluated COD and SS removal performance and power generation, and compared with those of MFCs equipped with Pt-based air-cathodes (MFC-Pts).

## **3.2 Materials and Methods**

### **3.2.1 MFC configuration and operation**

The serpentine up-flow air-cathode MFC was made from an acrylate block ( $20 \times 18 \times 3$  cm) and composed of the serpentine flow field and MFC system (**Fig. 3.1a**). The serpentine up-flow field consists of 3 slightly inclined ribs and 4 flow channels (**Fig. 3.2**). Total length of the serpentine up-flow channel is about 0.6 meter with a working volume of 300 mL (**Fig. 3.1a**). The MFC system consists of 4 anode graphite fiber brushes (2.2 cm (diameter)  $\times$  12 cm (length), Mill-Rose, Mentor, OH) installed in 4 flow channels, which are sandwiched with 2 separator electrode assembly (SEA) cells as previously described [17]. The SEA cell is composed of a carbon mesh anode ( $100 \times 100$  mm, Gaojieshi Graphite Products Co., Ltd., Fujian, China), separator (glass fiber or Nafion<sup>®</sup>), and air-cathode (Pt-based air-cathodes or PVDF-based activated carbon (AC) air-cathodes). The inclined ribs facilitate the settlement of particulate matter and slide down the accumulated sludge smoothly.

In this study, two different anode electrode types (graphite fiber brushes and carbon meshes) were used to provide sufficient surface area for biomass attachment, which facilitates COD and SS removal and electricity generation. In addition, biofilms attached on the carbon meshes create anoxic environment (a trace amount of oxygen may diffuse into the MFC through the air-cathode), which also facilitates electricity generation.

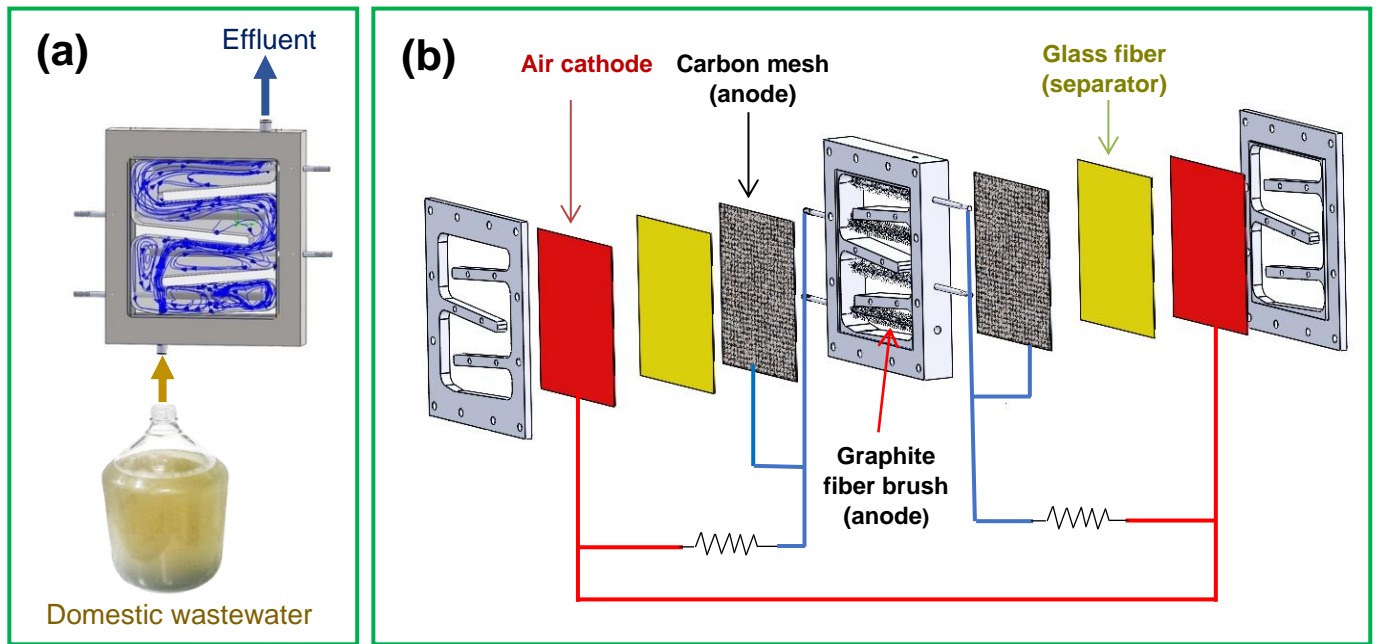
Two identical MFCs were constructed with Pt-based air-cathodes (termed as MFC-Pt-1 and -2) and PVDF-based activated carbon (AC) air-cathodes (termed as MFC-PVDF/AC-1 and -2),

respectively. The Pt-based air-cathode was a commercially available carbon paper containing Pt catalysis (10 cm × 10 cm, 0.3 mg Pt cm<sup>-2</sup>, Fuel cell store company, USA) with Nafion 117<sup>®</sup> as a separator. The PVDF-based activated carbon (AC) air-cathodes (10 cm × 10 cm) were fabricated by spreading 10% (w/v) PVDF solution containing 26.5 mg/cm<sup>2</sup> of AC (Norit<sup>®</sup> SX-Plus, Holland) and 8.8 mg/cm<sup>2</sup> of carbon black (CB) (Vulcan XC-72, Cabot Corporation, USA) directly onto a stainless steel mesh (1mm × 1mm, type 304, Eggs<sup>®</sup>, TAIHO, Co, Japan) as previously described [18]. The anodes and cathodes of the MFC-PVDF/ACs were separated by a glass fiber (1 mm thick and 24 mg / cm<sup>2</sup>, SAKAI SANGYO. Co., LTD, Japan) [19] (**Fig. 3.1b**).

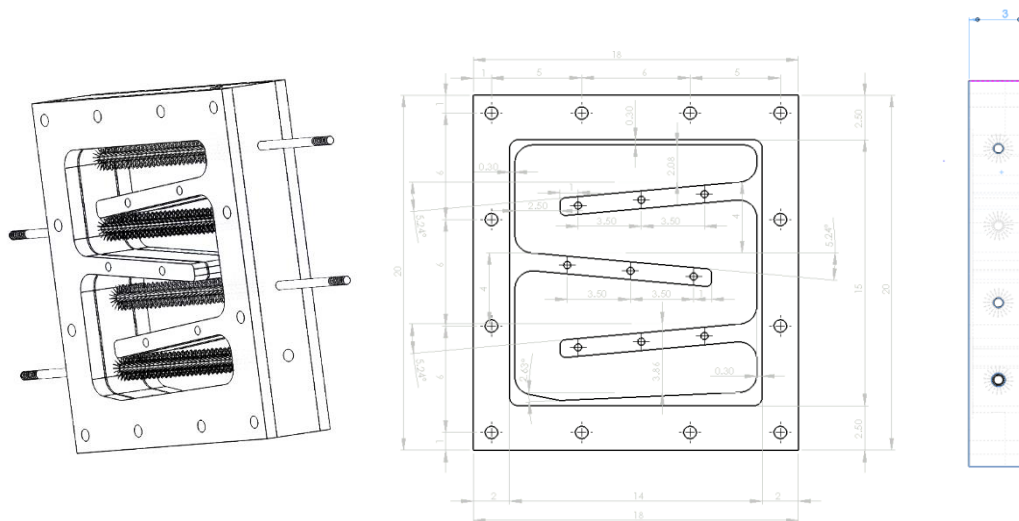
Individual MFCs were inoculated with activated sludge obtained from the Sapporo Sosei wastewater treatment plant (Sapporo, Japan) and continuously fed with the primary clarifier effluent (hereinafter referred to as domestic wastewater) at an HRT of 1.5 hr. The domestic wastewater was collected weekly and stored in the cold room at 4 °C prior to use. The domestic wastewater was kept in a refrigerator (4 °C) during operation and continuously fed to the MFCs by a peristaltic pump (ISMATEC<sup>®</sup> IPC, Germany). The external resistances for individual MFCs were varied in a range of 10 - 1,000 Ω to investigate the effect of external resistance on COD and SS removal performance. All MFCs were operated at room temperature (23 °C).

In this study, two different anode electrode types (graphite fiber brushes and carbon meshes) were used to provide sufficient surface area for biomass attachment, which facilitates COD and SS removal and electricity generation. In addition, biofilms attached on the carbon meshes create anoxic environment (a trace amount of oxygen may diffuse into the MFC through the air-cathode), which also facilitates electricity generation.





**Fig 3. 1:** Schematic of a serpentine up-flow air-cathode MFC (a) and separator assembly component of the air-cathode MFC and electrical wiring configuration (b).



**Fig 3. 2:** Schematic of a serpentine up-flow air-cathode MFC architecture

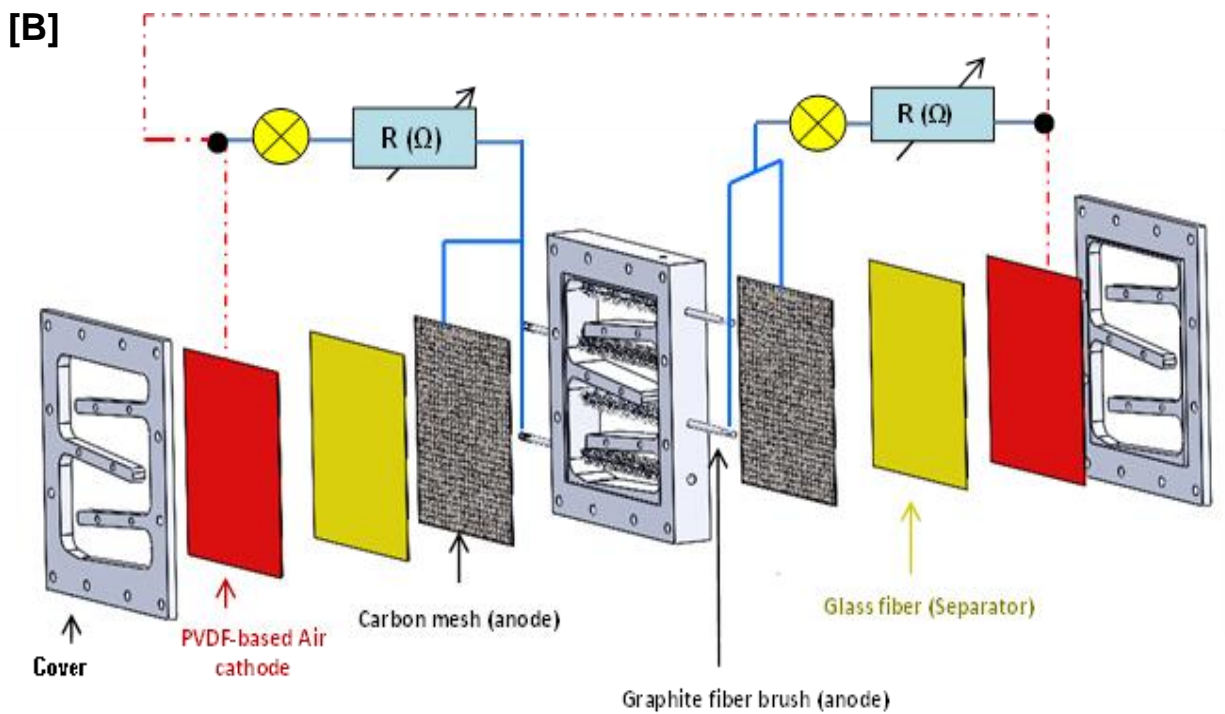
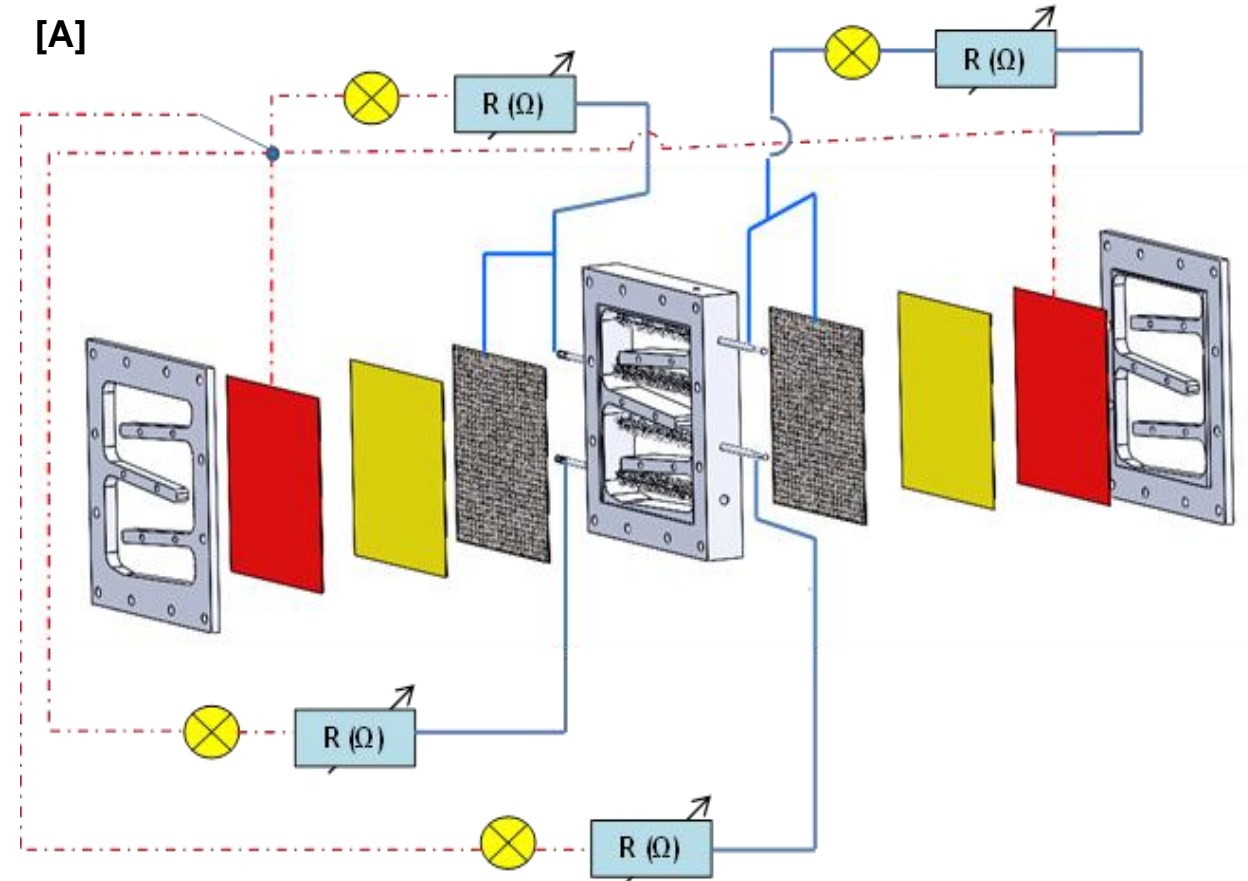


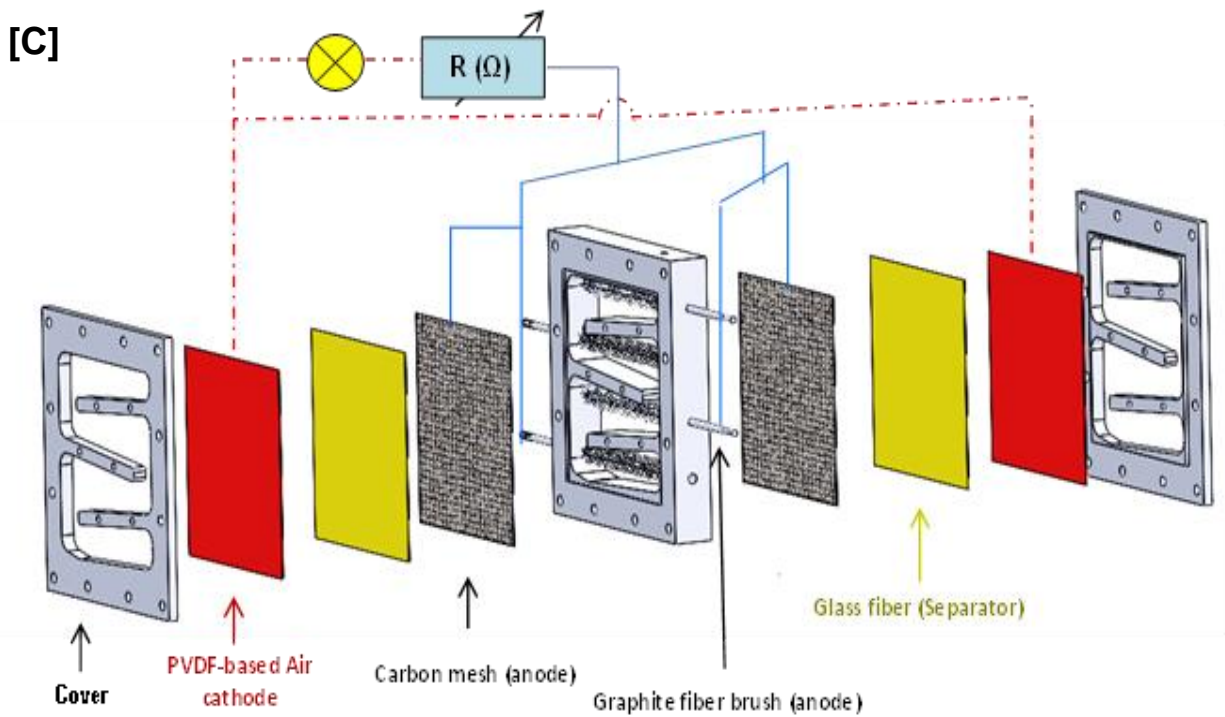
Two identical MFCs were constructed with Pt-based air-cathodes (termed as MFC-Pt-1 and -2) and PVDF-based activated carbon (AC) air-cathodes (termed as MFC-PVDF/AC-1 and -2), respectively. The Pt-based air-cathode was a commercially available carbon paper containing Pt catalysis ( $10\text{ cm} \times 10\text{ cm}$ ,  $0.3\text{ mg Pt cm}^{-2}$ , Fuel cell store company, USA) with Nafion 117<sup>®</sup> as a separator. The PVDF-based activated carbon (AC) air-cathodes ( $10\text{ cm} \times 10\text{ cm}$ ) were fabricated by spreading 10% (w/v) PVDF solution containing  $26.5\text{ mg/cm}^2$  of AC (Norit<sup>®</sup> SX-Plus, Holland) and  $8.8\text{ mg/cm}^2$  of Carbon Black (CB) (Vulcan XC-72, Cabot Corporation, USA) directly onto a stainless steel mesh ( $1\text{mm} \times 1\text{mm}$ , type 304, Eggs<sup>®</sup>, TAIHO, Co, Japan) as previously described [18]. The anodes and cathodes of the MFC-PVDF/ACs were separated by a glass fiber (1 mm thick and  $24\text{ mg/cm}^2$ , SAKAI SANGYO. Co., LTD, Japan (**Fig. 3.1b**) [19].

Individual MFCs were inoculated with activated sludge obtained from the Sapporo Sosei wastewater treatment plant (Sapporo, Japan) and continuously fed with the primary clarifier effluent (hereinafter referred to as domestic wastewater) at an HRT of 1.5 hr. The domestic wastewater was collected weekly and stored in the cold room at  $4\text{ }^{\circ}\text{C}$  prior to use. The domestic wastewater was kept in a refrigerator ( $4\text{ }^{\circ}\text{C}$ ) during operation and continuously fed to the MFCs by a peristaltic pump (ISMATEC<sup>®</sup> IPC, Germany). The external resistances for individual MFCs were varied in a range of  $10 - 1,000\ \Omega$  to investigate the effect of external resistance on COD and SS removal performance. All MFCs were operated at room temperature ( $23\text{ }^{\circ}\text{C}$ ).

During the startup period (day-5), we tested three types of anode-cathode electrical wiring connections (termed as connection [A], [B] and [C], respectively in **Fig. 3.3**. Briefly, connection [A]: one graphite fiber brush anode and a carbon mesh anode were wired together and then connected with an air-cathode. Another graphite fiber brush anode was directly connected with an air-cathode. [B]: two graphite fiber brush anodes and a carbon mesh anode were wired together

and then connected with an air-cathode, respectively. [C]: all anodic materials were wired together first and then connected with two air-cathodes. To find the best electrical connection that generates the highest current, the polarization tests were conducted using MFC-Pt-2 and MFC-PVDF/AC-2 with three types of electrical connections ([A], [B] and [C], respectively).





**Fig 3. 3 :** Illustrations of three different electrical wiring connections of MFCs. **[A]:** One graphite fiber brush anode and a carbon mesh anode were wired together and the connected with an air-cathode. Another graphite fiber brush anode was directly connected with an air-cathode. **[B]:** Two graphite fiber brush anodes and a carbon mesh anode were wired together and then connected with an air-cathode, respectively. **[C]:** All anodic materials were wired together first and then connected with two-sided air-cathodes.

### 3.2.2 Measurement and calculations

Total COD (tCOD) and soluble COD (sCOD) concentrations were measured using HACH COD digestion vials (high range: 20 - 1500 mg/L) and a DR 2400 spectroscopy (HACH, Loveland, Co) after the sample was filtered through a 0.45  $\mu\text{m}$ -pore-size membrane filter (ADVANTEC<sup>®</sup>, Japan) (Table 3.1). The concentrations of suspended solids (SS) and volatile suspended solids (VSS) in influent and effluent were measured according to the standard method for the examination of water and wastewater [20].

**Table 3. 1** Summary of physico-chemical properties of the domestic wastewater used in this study and average water quality of individual MFC effluents.

	Influent	Effluent			
		MFC-Pt-1	MFC-Pt-2	MFC-PVDF/AC-1	MFC-PVDF/AC-2
tCOD (mg/L)	410 $\pm$ 43	94 $\pm$ 46	102 $\pm$ 60	102 $\pm$ 61	91 $\pm$ 45
sCOD (mg/L)	164 $\pm$ 40	60 $\pm$ 26	66 $\pm$ 28	64 $\pm$ 29	59 $\pm$ 25
pCOD (mg/L)	247 $\pm$ 39	34 $\pm$ 27	36 $\pm$ 36	39 $\pm$ 39	32 $\pm$ 28
SS (mg/L)	308 $\pm$ 125	19 $\pm$ 9	15 $\pm$ 8	18 $\pm$ 10	16 $\pm$ 5
VSS (mg/L)	249 $\pm$ 111	16 $\pm$ 7	13 $\pm$ 7	15 $\pm$ 8	12 $\pm$ 6
Conductivity (mS/m)	63 $\pm$ 16	53 $\pm$ 15	62 $\pm$ 15	53 $\pm$ 14	51 $\pm$ 15
pH	6.8 $\pm$ 0.3	6.8 $\pm$ 0.4	6.7 $\pm$ 0.30	6.8 $\pm$ 0.2	6.7 $\pm$ 0.3

tCOD: total COD, sCOD: soluble COD, pCOD: particulate COD, SS: suspended solids, VSS: volatile suspended solids.

Current (I) and voltage (V) were measured at 30 min intervals using a data logger using a data logger (Agilent 34970A) and recorded in a personal computer. After confirming stable current generation and COD removal performance, the polarization tests were conducted only when

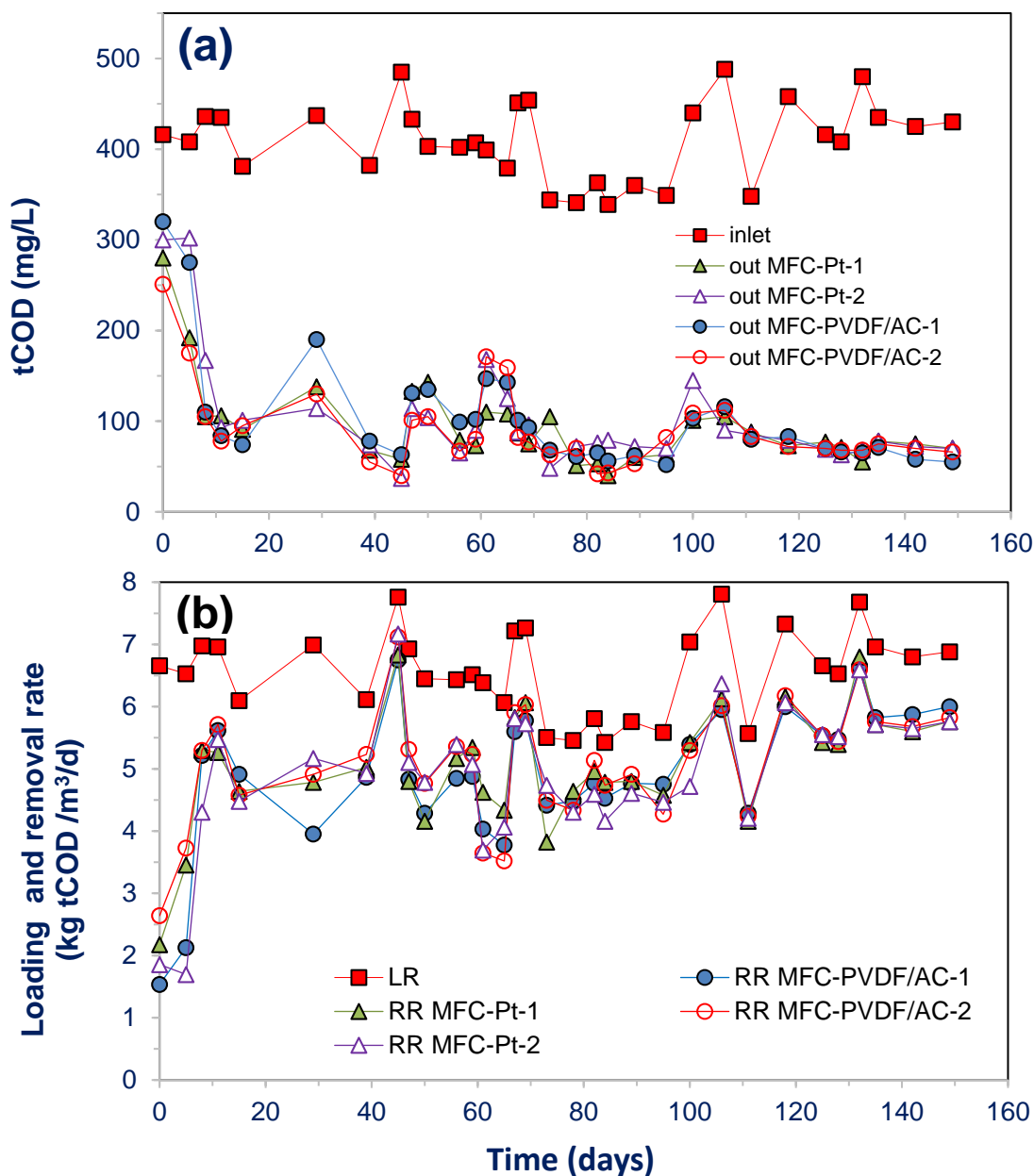
influent COD concentrations were over 400 mg/L to avoid the influences of COD loading rate limitation on electrochemical analysis [21]. Current densities ( $I_D$ ) and power densities ( $P_D$ ) were normalized to the MFC working volume [22]. The Coulombic efficiency (CE), defined as the fractional recovery of electrons from the substrate was calculated for continuous flow through the system based on the current generated under steady conditions as  $CE (\%) = C_t / C_{th} \times 100$ , where  $C_t$  was the total coulombs calculated by integrating the current over time ( $C_t = \int I \Delta t$ , where  $\Delta t$  is the time interval of one HRT), and  $C_{th}$  was the theoretical amount of coulombs available based on the COD removed in the MFC, calculated as  $C_{th} = Fb[\text{COD}_{in} - \text{COD}_t]Q \Delta t/M$ , where  $F$  is a Faraday's constant,  $b=4$  the number of exchanged electrons / mol  $O_2$ ,  $Q$  is the flow rate, and  $M=32$  the molecular weight of oxygen [22]. For polarization test, the voltage (V) – current (I), power (W) – current (I), and electrode potential (E) – I curves of the individual MFCs were determined by step-wisely changing the external resistance from 1,000 to 10  $\Omega$  with an Ag/AgCl reference electrode (RE-1B,  $E_0=195$  mV vs RHE, ALS Co, Japan).

### 3.3 Results and discussion

#### 3.3.1 COD removal

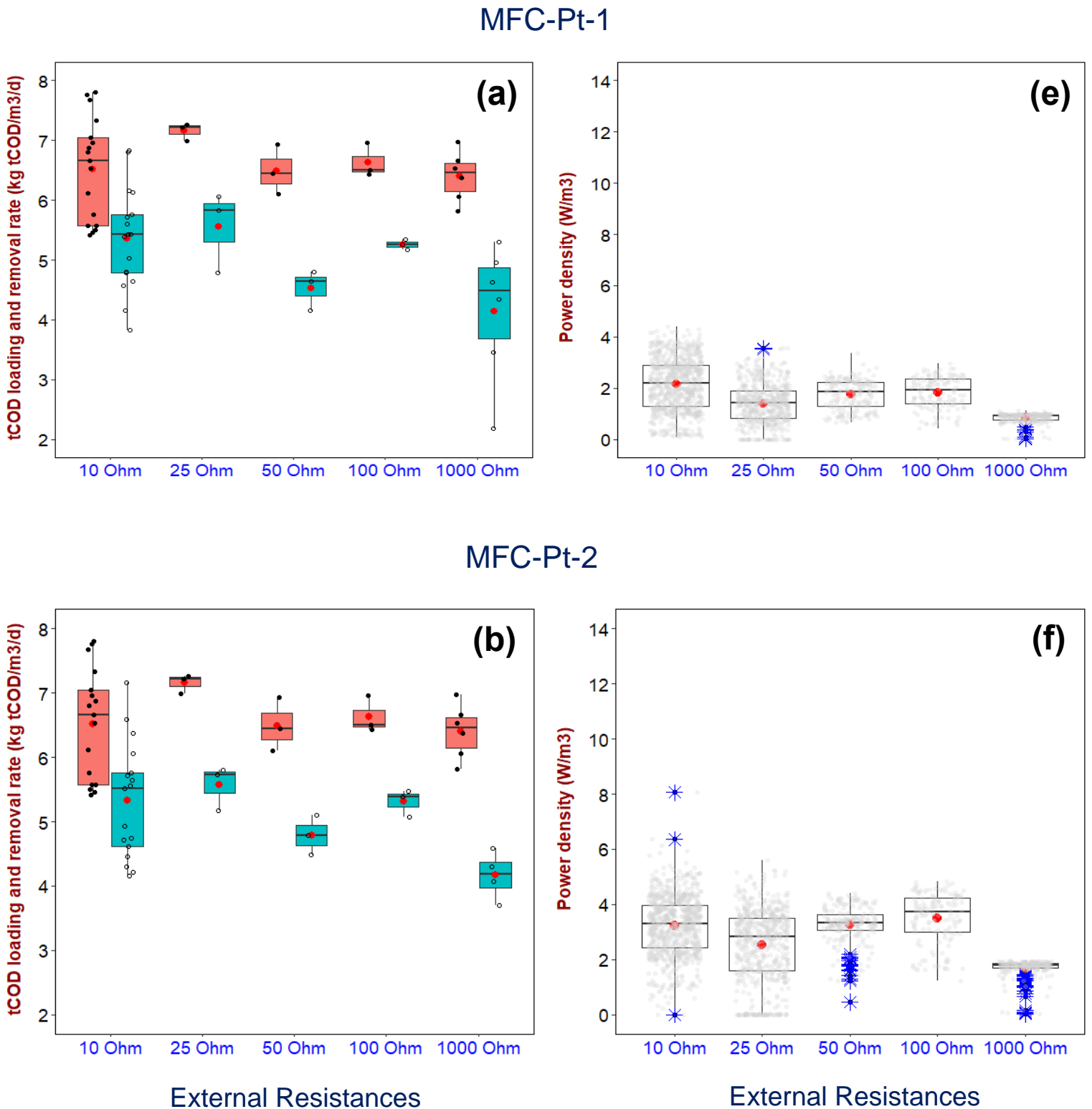
All MFCs were fed with real domestic wastewater at a loading rate of 5.4 -7.8 kg-tCOD/m<sup>3</sup>/d. The tCOD removal rates rapidly increased to approximately 5.0 kg-tCOD/m<sup>3</sup>/d for the initial 2 weeks. Accordingly, the effluent tCOD concentrations of each MFC were in the range of 55 - 88 mg/L despite large variation of influent tCOD concentrations (380 - 480 mg/L) after about 80 days (**Fig. 3.4a**). Average tCOD removal rates during the entire operational period of the MFC-PVDF/AC-1 and -2 were  $4.93 \pm 1.11$  kg-tCOD/m<sup>3</sup>/d and  $5.11 \pm 0.94$  kg-tCOD/m<sup>3</sup>/d, respectively, which were comparable to those of MFC-Pt-1 ( $5.06 \pm 0.94$  kg-tCOD/m<sup>3</sup>/d) and MFC-Pt-2 ( $4.93 \pm$

1.14 kg-tCOD/m<sup>3</sup>/d) (**Fig. 3.4b**). It should be noted that the PVDF-based AC air-cathode is easily manufactured and much less expensive than Pt-based air-cathode and has comparable COD removal rates. This suggests that MFC-PVDF/ACs could be sufficient enough for the treatment of low strength domestic wastewater in practice.



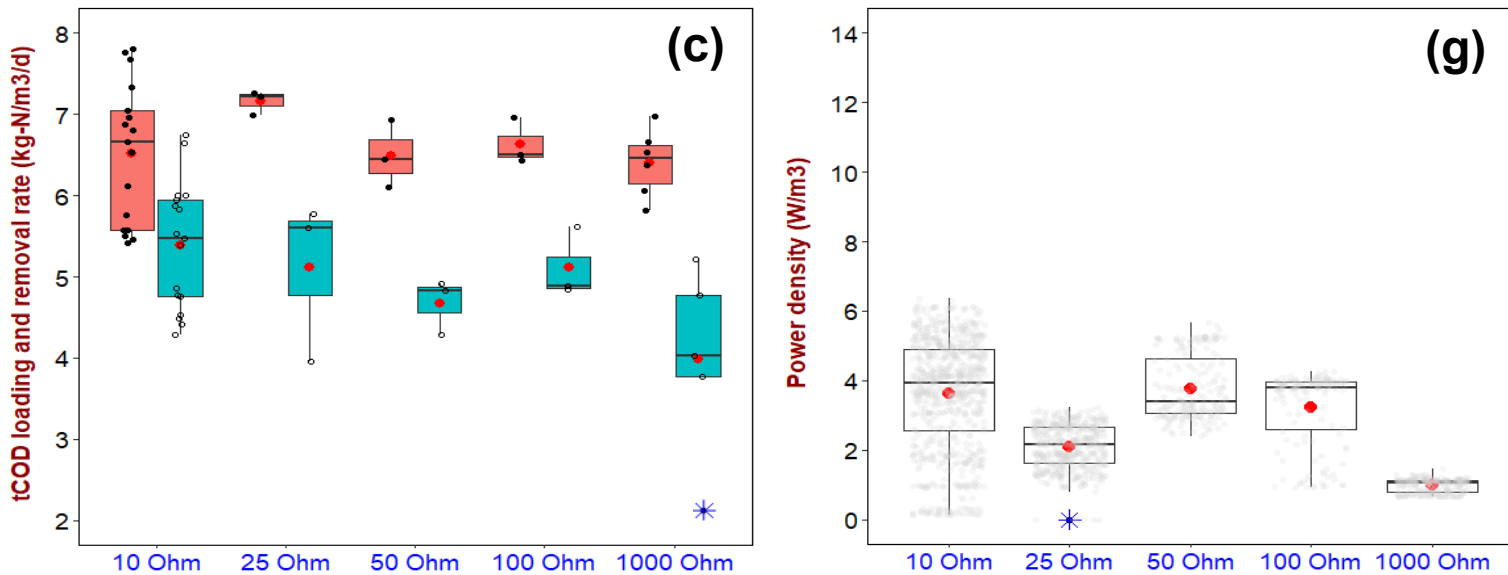
**Fig 3. 4 :** (a) Time course of total COD (tCOD) concentrations in influent and effluents. Average influent pCOD / tCOD ratio =  $0.6 \pm 0.07$  and effluent pCOD / tCOD ratio =  $0.37 \pm 0.16$  (n=32). (b) Time course of tCOD loading and removal rates. All MFCs were operated at 1.5h-HRT. LR = loading rate, RR = removal rate. tCOD= total COD, pCOD= particulate COD.

The external resistance value was changed to investigate its effect on the tCOD removal rate and power generation. When 1,000  $\Omega$  was applied, all the MFCs achieved relatively low tCOD removal rates (4.3 - 5.3 kg-tCOD/m<sup>3</sup>/d) and power densities (< 2.0 W/m<sup>3</sup>) (**Fig. 3.5**).

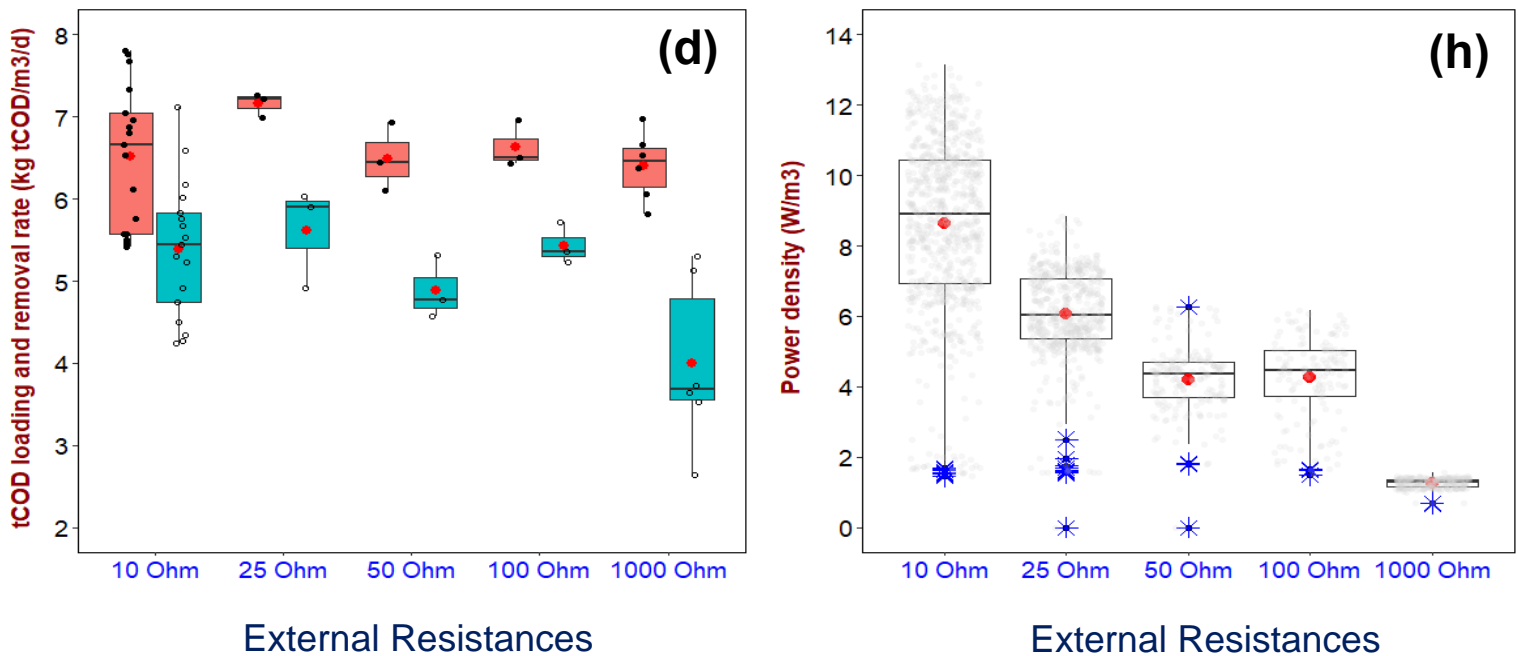




### MFC-PVDF/AC-1



### MFC-PVDF/AC-2



**Fig 3.5 :** (a-d) the red and blue box plots represent tCOD loading and removal rates against applied external resistances. (e-h) the white box plots represent the power densities against the external resistances. Black dots and open circles represent the data points of tCOD loading rate and tCOD removal rate, respectively (a-d). Grey dots represent the data points of power density. Red dots represent the mean values, blue asterisks represent the outliers. The bottom, medium and top horizontal lines represent the 1<sup>st</sup> quartile, the median and the 3<sup>rd</sup> quartile, respectively. The down and up whiskers represent the minimum and maximum value, respectively.

However, the tCOD removal rate and power density increased with decreasing the external resistance values. The highest tCOD removal rate of 7.12 kg-tCOD/m<sup>3</sup>/d (92 % of COD removal) was achieved with the lowest external resistance (10 Ω) in MFC-PVDF/AC-2, which were comparable to that of MFC-Pt-2 (7.2 kg-tCOD/m<sup>3</sup>/d, 92 % of COD removal). The tCOD removal rates at 10 Ω were about 1.5-fold higher than those at 1000 Ω. This indicates that reducing the external resistance accelerated bacterial exoelectrogenic activity (current generation) and consequently increased tCOD removal rate [23]. To our best knowledge, MFC-PVDF/AC-2 achieved an overall average tCOD removal rate of 5.11 ± 0.94 kg-tCOD/m<sup>3</sup>/d, which is the highest among air-cathode MFCs treating real domestic wastewater reported so far (**Table 3.2**).

The power density (3.96 ± 3.01 W/m<sup>3</sup>) were within the middle range of the previously reported values. The effluent tCOD concentrations were less than 80 mg/L (Fig. 4a), which is a typical range of effluent quality of conventional activated sludge systems [24]. The high COD removal rate of 13.93 kg-tCOD/m<sup>3</sup>/d (26% COD removal) with power density of 12.8 W/m<sup>3</sup> were reported using a relatively small air-cathode MFC reactor (0.028 L) with the external resistance of 500 Ω operated at a short HRT (0.22 h) [25] (**Table 3.2**).

Relatively high tCOD removal rates of these MFCs could be explained by the long serpentine up-flow path (ca. 60 cm) with 4 graphite fiber brush anodes (**Fig. 3.1a**). The graphite fiber brush anodes provide large surface area for attachment of exoelectrogenic bacteria and also act as physical filters [26] to remove suspended solids (SS) from wastewater as mentioned below. Thus, the combination of both physical filtration and biological oxidation is largely attributed to the high and stable tCOD and SS removal rates of MFC-PVDF/ACs at a relatively short HRT (1.5 h).

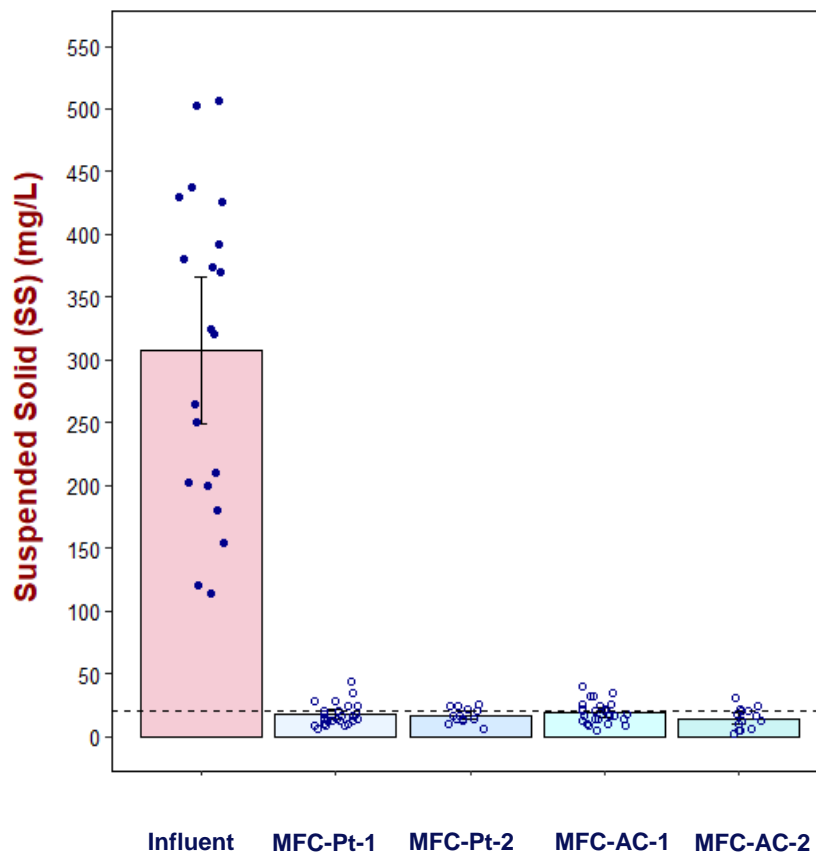
**Table 3. 2** : Performance of air cathode MFCs treating domestic wastewater

MFC type	working volume (L)	HRT (h)	R ( $\Omega$ )	COD <sub>in</sub> (mg/L)	COD <sub>out</sub> (mg/L)	COD <sub>rem</sub> (%)	COD RR (kg-tCOD/m <sup>3</sup> /d)	CE (%)	I <sub>D mean</sub> (A/m <sup>3</sup> )	P <sub>D mean</sub> (W/m <sup>3</sup> )	Ref.
Plug flow MFC (stack)	250	144	1	333.33	70±17	79	0.04	3~5	1.74	0.47	[2]
Pilot-scale MFC	44.8	22	75	118	90	24	0.031	24.8	na	0.220	[3]
MAC-MFCs	20	5 ~20	100	100~1000	30~80	66 - 88	0.4 ~0.55	0.3	na.	0.16 ~ 0.2	[27]
SEA-MFC	6.1	4	20	~500	100-200	57 ± 15	1.71	28	na.	6.0 ± 0.4	[21]
air-cathode MFC	0.14	4.4	200	~400	>100	48.3	na	18~29	na	12.3	[28]
air-cathode MFC	0.028	0.22	500	500	371	25.8	13.93	1.7	~50	12.8	[25]
SEA-MFC	0.15	0.5	50	144 ± 18	~60	34 ± 5 (max =42)	2.90	na.	60 ± 33	12.9 ± 2.9	[29]
SEA-MFC	5.7	6 ~ 8	50	108	20~35	66-80	0.23 ~ 0.344	< 6	na	0.350 ~0.534	[30]
SEA-MFC	0.1	2	100	~400	218	~45.5	2.18	45.1 ±1.0	na	18.84	[17]
MFC (stack)	0.028	0.33	na	340~446	~200.5	44	11.3	1.8~13	28.3	12.8	[31]
ABMFC	1.6	192~288	1000	237.78 ± 7.65	44.16 ± 1.91	80.21	na	17.01	na	0.01	[32]
UBEF	0.184	5.52~6.72	1000	120~450	na	89	na	0.25~1.51	0.31±0.02	0.103	[33]
MFC-Pt-1	0.3	1.5	10	421± 64	84.6 ± 26.2	79.3 ± 6.3	5.06±0.94	3.3	9.72±6.04	1.38±0.86	This study
MFC-Pt-2	0.3	1.5	10	421± 64	89.1 ± 30.6	78.2± 7.3	4.93±1.14	3.4	11.69±8.24	1.82±1.24	This study
MFC-PVDF/AC-1	0.3	1.5	10	421± 64	89.4 ± 33.3	78.2± 7.7	4.93±1.11	4.5	14.55±10.29	2.29±1.88	This study
MFC-PVDF/AC- 2	0.3	1.5	10	421± 64	83 ± 30.9	79.7±7.7	5.11±0.94	7.0	21.48±16.97	3.96±3.01	This study

SEA-MFC: Separator electrode assembly MFC, MAC-MFC: multi-anode/cathode microbial fuel cells, ABMFC: algae biofilm microbial fuel cell, UBEF: up-flow bioelectrochemical filter, na.: not available, P<sub>D</sub>: power density, I<sub>D mean</sub>: mean current density, CE: Coulombic efficiency, COD RR: COD removal rate, R : applied external resistance ( $\Omega$ ) .

### 3.3.2 Suspended solids (SS) removal

Although the influent suspended solids (SS) concentrations fluctuated widely, low and stable effluent SS concentrations ( $< 20$  mg SS/L) were achieved for all MFCs (**Fig. 3.6**), which meet the Japanese discharge standards. SS and VSS removal efficiencies were not significantly different at various applied external resistances, indicating that SS and VSS were mainly removed by physical filtration of the graphite fiber brush anodes. In addition, the up-flow water flow path promotes gravity sedimentation and prevents re-suspension of SS, which provides good solid-liquid separation properties [34].



**Fig 3. 6 :** Average influent and effluent suspended solids (SS) concentrations. Dots and circles represent data points ( $n=20$ ), a horizontal dotted line denotes the Japanese suspended solid discharge requirement, and vertical bars are the standard errors. Influent VSS / SS ratio =  $0.80 \pm 0.09$ , MFCs effluent VSS / SS ratio =  $0.81 \pm 0.22$ . VSS= volatile suspended solid.

The high removal efficiencies of SS and VSS (>90% removal efficiency) were superior to those reported so far for MFCs treating domestic wastewater. For example, SS removal efficiency of ca.70% was achieved for a 20-L pilot-scale up-flow air-cathode MFC treating domestic wastewater operated at 5h-HRT [27]. During more than 6-month operation, we did not observe any excess sludge clogging event in all the MFCs. According to the influent and effluent SS concentrations and flow rate, it could be theoretically estimated that approximately 215 g of SS (correspondingly 716 g-SS/L as mixed liquor SS) were entrapped in a MFC unit with 300 mL of a working volume during 160-day operation. Such extremely high effluent SS concentrations and massive sludge accumulation in all the MFCs were not observed during the entire operation.

In addition, according to steady-state influent and effluent soluble COD (sCOD) concentrations and effluent volatile SS (VSS) concentrations, biomass growth yields in MFC-Pt-1 MFC-Pt-2, MFC-PVDF/AC-1 and MFC-PVDF/AC-2 were estimated to 0.11, 0.11, 0.10 and 0.10 g-VSS/g-sCOD removed, respectively. These low biomass yield values were in accordance with the previous reported values (0.07 to 0.16 g-VSS/g-COD removed) [35], which is much less than typical values of the activated sludge (0.35 - 0.45 g-VSS/g COD removed). This clearly indicates that MFCs produced less biomass and the accumulated suspended solids were anoxically and/or bioelectrochemically oxidized.

### **3.3.3 Power generation**

The external resistance significantly influenced power and voltage generation during the startup (**Fig. 3.5 and 3.7**) With decreasing external resistance from 1,000  $\Omega$  to 10  $\Omega$ , the rapid evolution of power density was observed without lag times for all MFCs. Particularly, the MFC-PVDF/AC-2 generated the average power density of  $8.6 \pm 2.4$  W/m<sup>3</sup> at 10  $\Omega$ , which was much higher than

that of MFC-Pt-2 ( $23.2 \pm 1.1 \text{ W/m}^3$ ) (**Fig. 3.5**). In this study, higher tCOD removal rates and power densities were observed at  $10 \Omega$  in all MFCs. Therefore, all MFCs were operated with  $10 \Omega$  thereafter. Overall, MFC-PVDF/AC-1 and -2 produced average power densities of  $2.29 \pm 1.88 \text{ W/m}^3$  (current density  $14.55 \pm 10.29 \text{ A/m}^3$ ) and  $3.96 \pm 3.01 \text{ W/m}^3$  ( $21.48 \pm 16.97 \text{ A/m}^3$ ), while MFC-Pt-1 and -2 produced slightly lower power densities of  $1.38 \pm 0.86 \text{ W/m}^3$  ( $9.72 \pm 6.04 \text{ A/m}^3$ ) and  $1.82 \pm 1.24 \text{ W/m}^3$  ( $11.69 \pm 8.24 \text{ A/m}^3$ ). Both the MFC-PVDF/ACs generated the higher power density than MFC-Pts. However, the power densities and current densities gradually decreased in all MFCs, respectively (**Fig. 3.7**). The main reason could be deterioration of the cathode performance due to biofilm formation on the water side and inorganic chemical precipitation (e.g., NaOH) on the air side of cathodes after the long-term operation (**Fig. 3.8**). Similar power decay during the long-term operation of activated carbon air-cathode was reported previously [36–38]. In order to maintain the high MFC power generation, chemical precipitation on the air side of the PVDF/AC cathodes were periodically washed with tap water, which led to quick recovery of the power generation. However, chemical precipitation occurred in a relatively short time. The periodical cathode washing resulted in considerable variations in power densities observed in both MFC-PVDF/ACs after 120 days (**Fig. 3.7b**).

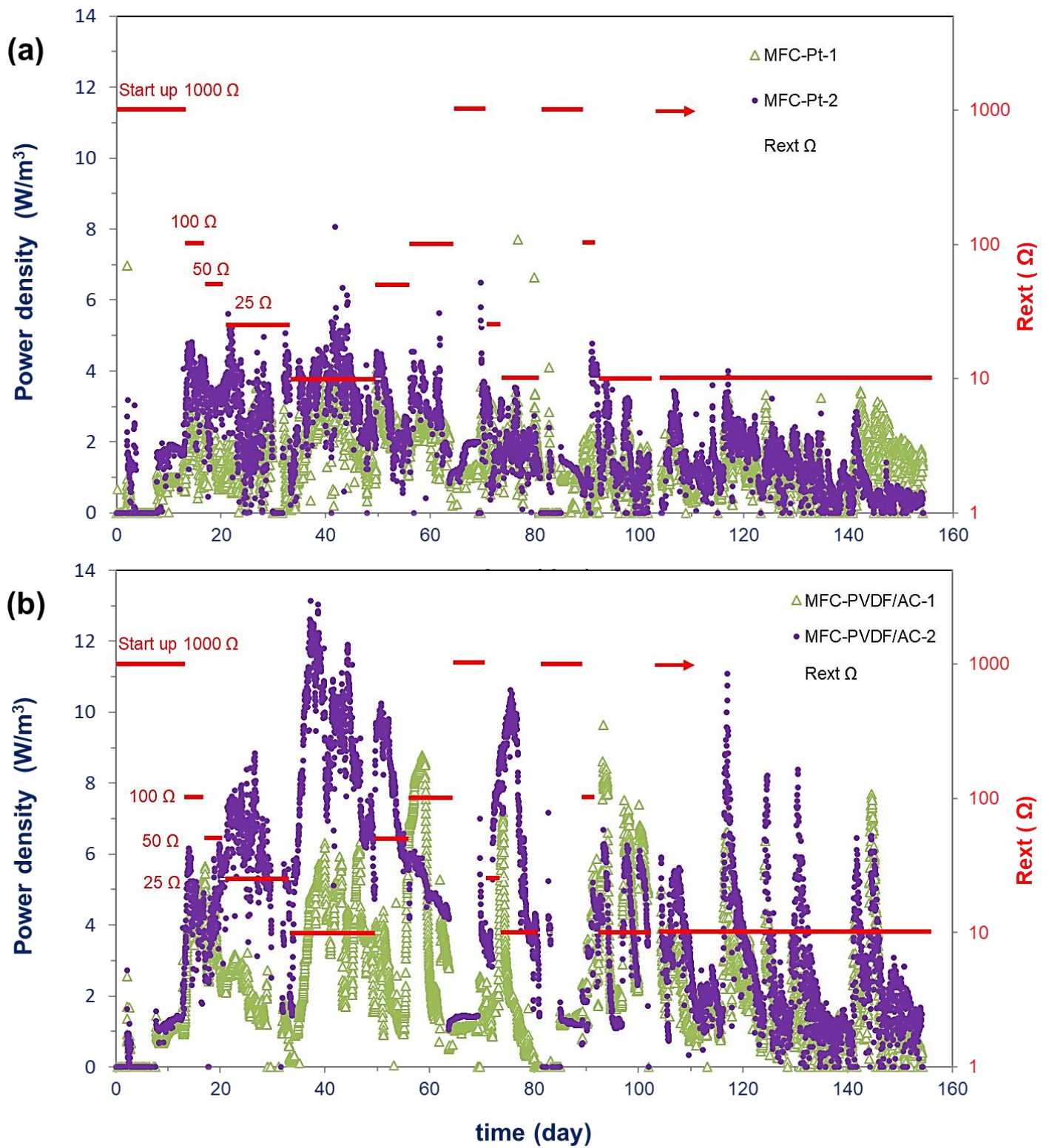
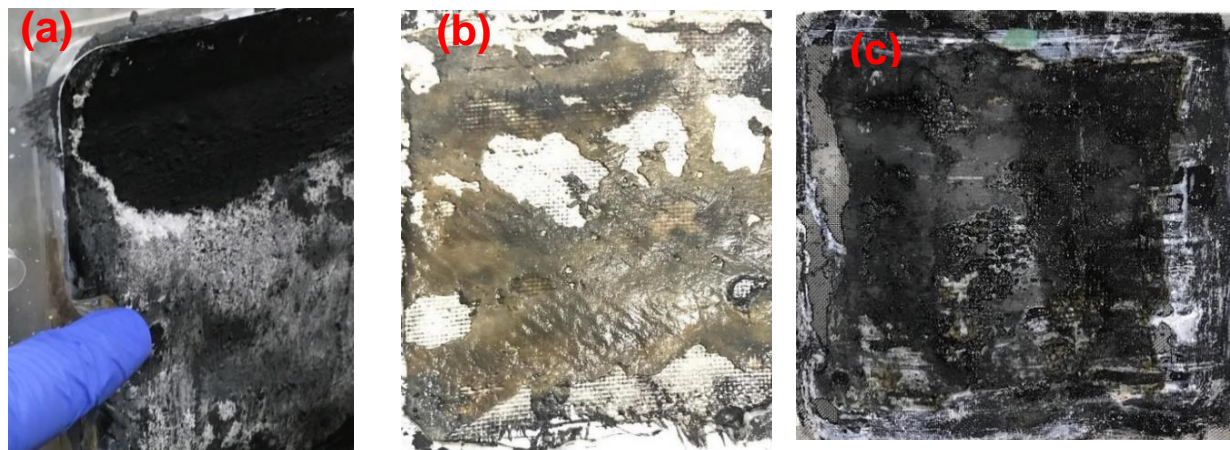


Fig 3. 7 : Time course of power densities of MFC-Pts (a) and MFC-PVDF/ACs (b).





**Fig 3. 8 :** (a) salt precipitation on the air side of PVDF-based air cathode, (b) biological fouling (biofilms) on separator, (c) biological fouling (biofilms) on the water side PVDF-based air cathode.

Similar power decay during the long-term operation of activated carbon air-cathode was reported previously [36–38]. In order to maintain the high MFC power generation, chemical precipitation on the air side of the PVDF/AC cathodes were periodically washed with tap water, which led to quick recovery of the power generation. However, chemical precipitation occurred in a relatively short time. The periodical cathode washing resulted in considerable variations in power densities observed in both MFC-PVDF/ACs after 120 days (**Fig. 3.7b**).

### 3.3.4 Polarization test

After acclimatization to 10  $\Omega$  of external resistance (after stable tCOD removal rate was confirmed around day 90), polarization tests were performed to evaluate the electrochemical performance of each MFC (**Fig. 3.9**). Despite making two identical MFC-Pts and MFC-PVDF/ACs and operating them under the same condition, the open circuit potential (OCP) values were different; +275 mV (vs. Ag/AgCl) for MFC-Pt-1, +224 mV for MFC-Pt-2, +100 mV for MFC-PVDF/AC-1 and + 160 mV for MFC-PVDF/AC-2, respectively (**Fig. 3.9c and 3.9d**). The OCP values of MFC-Pts were higher than those of MFC-PVDF/ACs, because Pt-based cathode

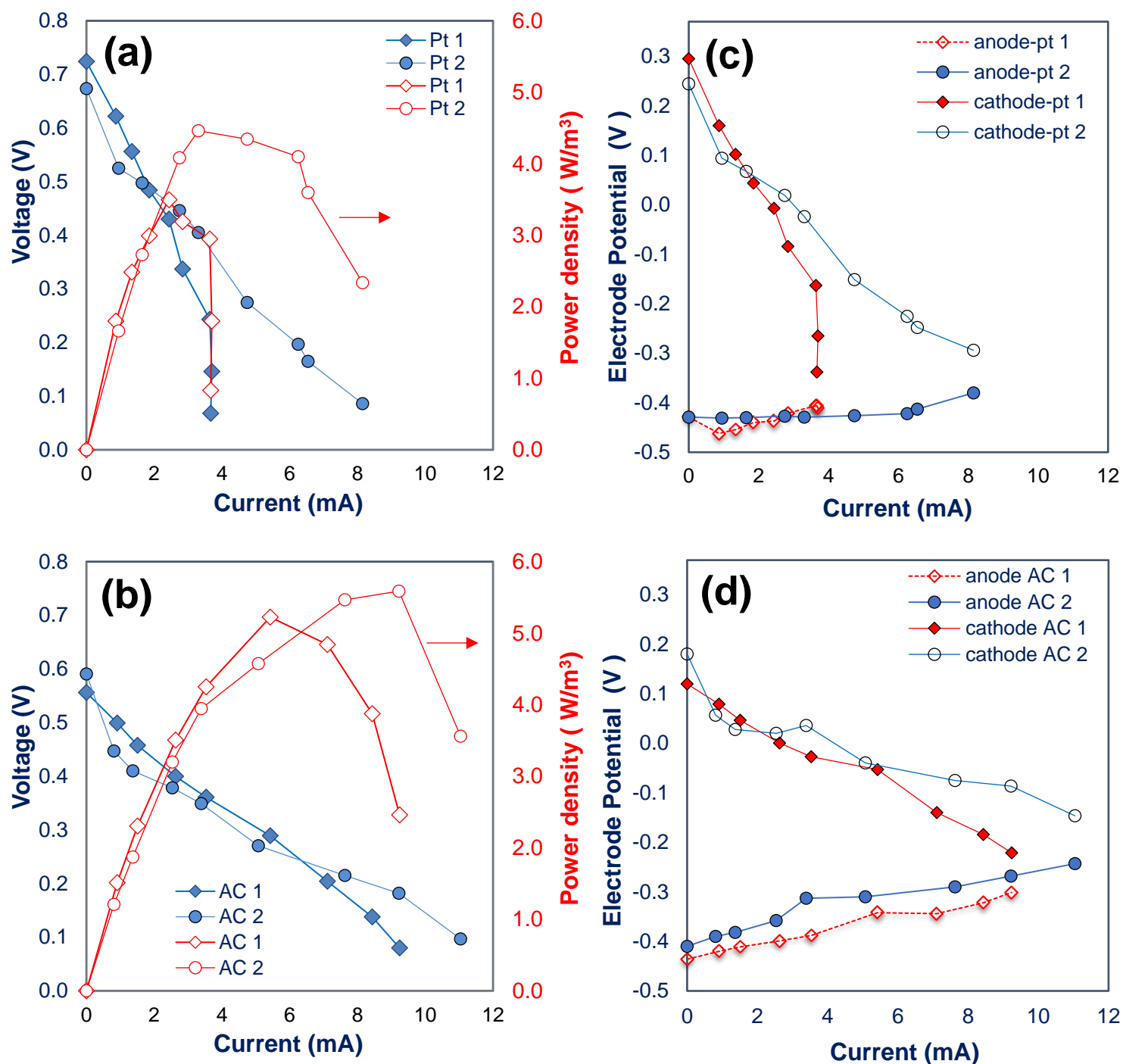


has higher oxygen reduction reaction activity than carbon-based cathode [39]. The polarization data revealed that the maximum power (current) densities of MFC-Pt-1, MFC-Pt-2, MFC-PVDF/AC-1, and MFC-PVDF/AC-2 were 3.5 W/m<sup>3</sup> (12.3 A/m<sup>3</sup>), 4.5 W/ m<sup>3</sup> (27.2 A/m<sup>3</sup>), 5.2 W/m<sup>3</sup> (30.8 A/m<sup>3</sup>) and 5.6 W/m<sup>3</sup> (36.8 A/m<sup>3</sup>), respectively. Measurement of individual electrode potentials (**Fig. 3.10**) showed that the anode potentials were roughly in the same range in all MFCs, whereas the cathode exhibited a pronounced difference. Accordingly, the differences in the maximum power densities could result from the different cathode materials [40]. Thus, MFC-PVDF/AC-2 yielded the highest power and current densities, which was consistent with the time course of power generation data obtained during the continuous operation (**Fig. 3.7**). This is probably attributed to difference in the internal resistance ( $R_{\text{int}} = -\Delta E / \Delta I$ ), which is due to such as ohmic loss, activation loss, and mass transfer loss.

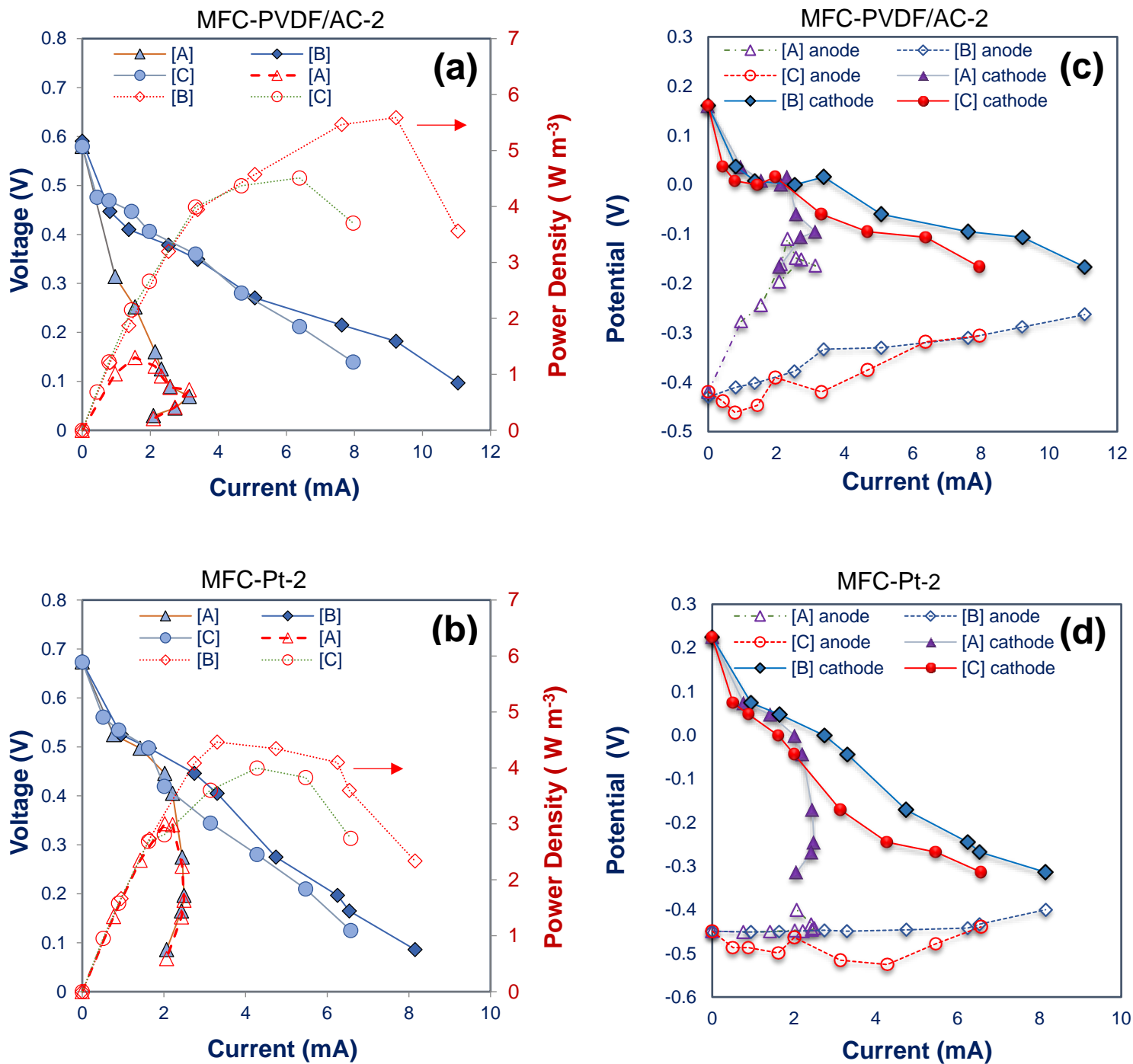
### **3.3.5 Optimization of electrical connection**

Polarization tests were also conducted using MFC-Pt-2 and MFC-PVDF/AC-2 with three types of electrical connections ([A], [B] and [C], **Fig. 3.3**) to find the best electrical connection structure. For MFC-PVDF/AC-2, the maximum power density of 5.7 W/ m<sup>3</sup> was obtained at 9.2 mA with the [B]-type electrical connection which was higher than those of [A]-type (1.5 W/m<sup>3</sup> at 1.3 mA) and [C]- type (4.5 W/m<sup>3</sup> at 6.4 mA) electrical connection, respectively (**Fig. 3.10**). The similar results were obtained for MFC-Pt-2. Furthermore, the internal resistance is closely related to the electrical connection structure. For example, the internal ohmic loss ( $R_{\text{int}}$ ) of [B]-type connection was 37  $\Omega$ , which was lower than the [A]-type (169  $\Omega$ ) and [C]-type (46  $\Omega$ ) connection, respectively. The increase of internal resistance was accompanied by a higher power overshoot [35], which was probably attributed to anodic kinetic limitation, specifically from electron depletion, rather than cathodic kinetic limitation [36]. The power overshoot observed in the [A]-

type electrical connection is due to a rapid increase of anode potential from  $-449$  mV to  $-150$  mV (vs. Ag/AgCl), as compared to the [B]-type connection which ranged between  $-449$  mV and  $-426$  mV (vs. Ag/AgCl). This result is consistent with the previous study reporting that the powers overshoot during the polarization test due to a rapid increase in the anode potential [37]. Since the [B]-type electrical connection yielded the highest power generation from domestic wastewater, it was implemented in all MFCs during the continuous operation.



**Fig 3. 9 :** Polarization tests of the MFCs. Power densities ( $\circ$  and  $\diamond$  symbol) with voltages ( $\blacklozenge$  and  $\bullet$  symbol) (a-b) and electrode potentials vs Ag/AgCl (c-d) of MFC-Pt-1 and -2 and MFC-PVDF/AC-1 and -2.



**Fig 3. 10 :** Polarization curves showing power densities ( $\Delta$ ,  $\circ$  and  $\diamond$ ) with voltages ( $\triangle$ ,  $\blacklozenge$  and  $\bullet$ ) (a-b) and electrodes potentials vs Ag/AgCl (c-d) of MFC-PVDF/AC-2 and MFC-Pt-2 with three different electrical connections. Based on the polarization tests, the electrical connection [B] exhibited the highest power density for both the MFCs.

### **3.3.6 Durability of cathode**

Air-cathodes must be watertight and durable so that MFC can be scaled-up without water leak. No water leakage was observed in both MFC-PVDF/AC during the entire 6-month operation, whereas frequent water leakages occurred in MFC-Pts in the later stage of operation (101, 120, 135, and 150 days) due to the breakage of Pt-based air-cathode. The possible reason could be the mechanical fatigue due to deformation induced by the inner water pressure during such a long-term operation. Indeed, the Pt-based air-cathode made of carbon paper was mechanically quite robust but tended to be brittle during the long-term operation with real domestic wastewater. This indicates that PVDF-based AC air-cathode is more durable and has better water pressure resistance than Pt-based air-cathode. Similarly, the high water pressure resistance of PVDF-based air-cathode was reported by Yang et al. (2014). In addition, the PVDF-based activated carbon air-cathode can be easily manufactured at room temperature [18].

## **3.4 Conclusions**

The PVDF-based activated carbon (AC) air-cathode MFC (MFC-PVDF/AC-2) could achieve a stable tCOD removal rate (average tCOD removal rate =  $5.11 \pm 0.94$  kg-tCOD /m<sup>3</sup>/d) and power density (average power density =  $3.96 \pm 3.01$  W/m<sup>3</sup>) with domestic wastewater as a substrate at 1.5-h HRT and ambient temperature (~23 °C). This performance was higher than those of the Pt-based air-cathode MFCs (MFC-Pts). In addition, the PVDF-based AC air-cathode is less expensive (\$ 0.0015 / cm<sup>2</sup>), more durable, and easy to manufacture than Pt-based air-cathode (\$ 2.15 / cm<sup>2</sup>).

The MFC-PVDF/ACs had excellent removal performance of suspended solids (SS) owing to the serpentine up-flow path, the physical filtering effect of the graphite fiber brush anodes and

biological oxidation by exoelectrogens. The clogging event did not occur during more than 6-month operation without carrying out excess sludge removal, suggesting no requirement of the costly sludge treatment process. Thus, the MFC/AC show excellent wastewater treatment and could be a cost-effective energy-saving domestic wastewater treatment process.

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## **Chapter 4**

# **Energy harvesting by serpentine up-flow MFCs equipped with PVDF-based activated carbon air-cathodes and a low voltage booster**

### **4.1 Introduction**

The microbial fuel cell (MFC) technology has been intensively researched in the recent decade because it offers a solution for environmental sustainability by simultaneously performing pollutant removal and energy production [1]. Despite the advantages of this technology in terms of wastewater treatment, the generated voltage output of the single MFC unit is too low ( $<0.5$  V) to be used directly used to drive a small electronic device such as LEDs (2 V), wireless microsensors (3.3V) for instance. One approach to increase the output voltage is to serially stack the MFCs unit [2]. However, this technique usually leads to the voltage reversal issue which decreases the voltage in stacked MFCs [3,4]. Another technical solution is the use of a Power Management System (PMS). A PMS is an electronic system designed to accumulate electrical energy and boost a low voltage output of a given power source into a high (usable) level [5].

To date, various commercially available or individually developed PMS have already proposed by several researchers to recover usable energy from MFC [4,6–10], and each PMS has its own application [8] and working voltages. However, it important highlight that several studies have reported that MFCs equipped with those existing PMSs can intermittently power small electronic load for only fractions of a second to several minutes [9]. Another disadvantage of the actual PMS is due to its conventional electronics components which are not compatible with the MFC technology [6]. For example, a diode or a (Metal-Oxide-Semiconductor Field-Effect Transistor) which usually compose the PMS system required a minimum of 0.7 V to run. Thus, for long-term energy harvesting application MFC need to be equipped with a customized PMS which is compatible with the low voltage output (<0.5V). to our knowledge, dedicated PMS for MFCs energy harvesting application has not been developed.

In this study, our objective is to develop such PMS compatible with MFC application. Therefore, we have continuously operated MFC-PVDF/ACs with real domestic wastewater for more than 6 months. Thereafter, we newly developed a low voltage booster (LVB) to increase the low output voltage of MFC-PVDF/AC to usable levels. The experimental results indicate that LVB system is compatible with the MFC output voltage and the integrated MFC-PVDF/AC and LVB system could be an inexpensive, durable and energy-saving (or recovering) primary wastewater treatment system.

## **4.2 Materials and method**

### **4.2.1 MFC configuration and operation**

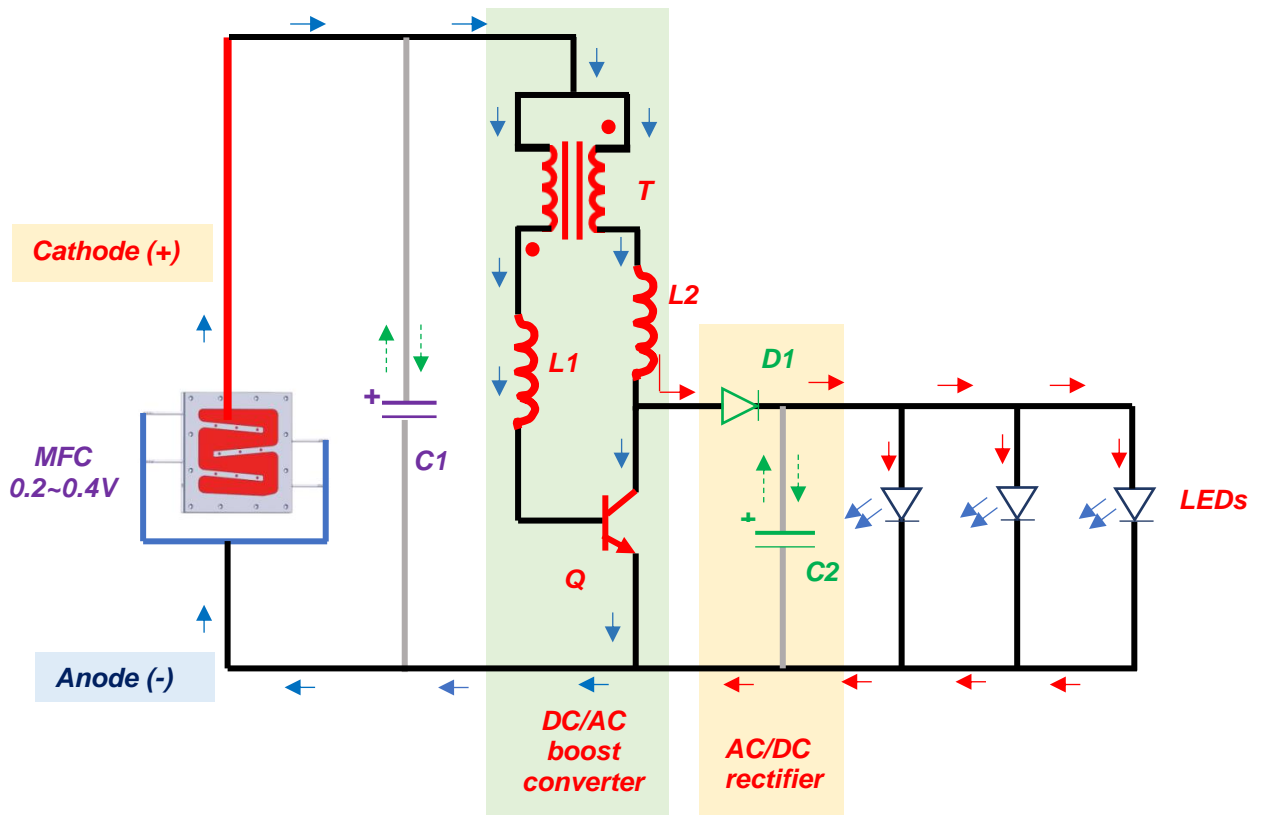
The serpentine up-flow air-cathode MFC was made from an acrylate block (20 × 18 × 3 cm) and composed of the serpentine flow field and MFC system previously described for domestic wastewater treatment. The serpentine up-flow field consists of 3 slightly inclined ribs and 4 flow channels. Two identical MFCs were constructed with PVDF-based activated carbon (AC) air-cathodes (termed as MFC-PVDF/AC-1 and -2), respectively. Individual MFCs were inoculated with activated sludge obtained from the Sapporo Sosei wastewater treatment plant (Sapporo, Japan) and continuously fed with the primary clarifier effluent (hereinafter referred to as domestic wastewater) at an HRT of 1.5 hr. The domestic wastewater was collected weekly and stored in the cold room at 4 °C prior using. The domestic wastewater was kept in a refrigerator (4 °C) during operation and continuously fed to the MFCs by a peristaltic pump (ISMATEC® IPC, Germany). All MFCs were operated at room temperature (23 °C).

### **4.2.2 Low voltage boosting system**

The low voltage output of MFCs was boosted by a newly made DC/DC low voltage booster (LVB) (**Fig. 4.1**). The LVB is a self-oscillating voltage booster which firstly converts a low voltage output from MFCs (*ie* Direct Current voltage or DC voltage) into alternating voltage (*ie* AC voltage) and then rectifies the boosted AC voltage to a high DC voltage. In this LVB electronic circuit, the bipolar junction transistor (BJT) STN851 acts as a fast switch turning ON and OFF the circuit at a high frequency. The NPN transistor STN851 was selected for this LVB circuit because

of its outstanding fast-switching speed and its ability to operate at low voltage [11] compared to others BJTs or metal-oxide-semiconductor field-effect transistors (MOSFETs) commonly used as a switch.

The low DC voltage output is boosted via a DC/AC voltage inverter circuit composed by a superfast switch NPN transistor (STN851) and inductors (Toroid ferrite coil inductor with double windings of 20 Turns and two axial inductors L1, L2 (680  $\mu$ H)) used to store and discharge energy into the circuit in the repeated circle. The repeated charge and discharge cycle of the inductors enable the ON- / OFF-state of the transistor, thus inducing a high AC voltage spike ( $>2$  V) and allow the electrical current flow through the diode D1 to light the LEDs. Afterwards, the boosted AC voltage is converted into DC voltage by the mean of the rectifier filter circuit (Diode rectifier D1: 1N4001, Capacitor C2: 10V/ 4.7 mF). The capacitor C1 is used as an electron buffer to store the electrical energy from a MFC. Current (I) and voltage (V) were measured at 30 min intervals using a data logger (Agilent 34970A) and recorded in a personal computer.

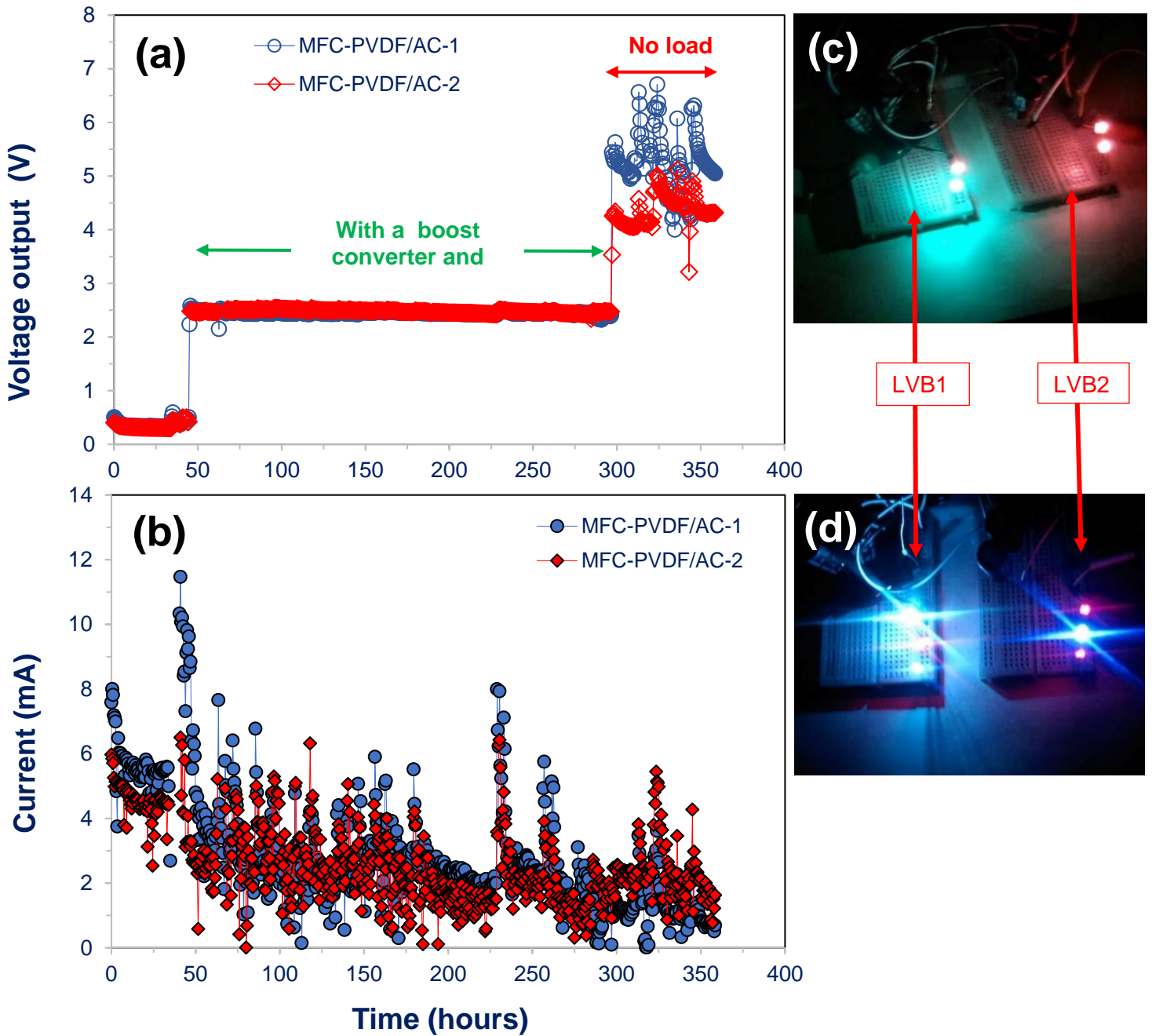


**Fig 4. 1 :** Schematic diagram of the homemade DC/DC Low Voltage Booster (LVB). C1 and C2 are polarized capacitors 10V / 4.7 mF, L1 and L2 are axial inductors (680  $\mu$ H), D is a diode rectifier 1N4001, Q is a superfast switch NPN transistor (STN851). T is a toroid ferrite coil inductor with double windings of 20 Turns. The blue arrows represent the conventional current flow when Q is ON, and the red arrow represent the conventional current flow when Q is OFF. The green dotted arrows represent the charge and discharge of capacitor C1 and C2.

### **4.3 Results and discussions**

Low voltage boosters (LVBs) were newly developed and connected to MFC-PVDF/AC-1 and -2, respectively to increase such low MFC output voltages. To visually demonstrate the enhancement of LVB output voltage, LED bulbs (2.2 V and 20 mA) were connected to each LVB as a load.

When a single voltage booster was connected to each MFC-PVDF/AC, respectively, the LVB output voltages increased instantaneously from  $< 0.4$  V to approximately 2.5 V and remained stable in both cases (**Fig. 4.2a**). This LVB output voltage became sufficient enough to turn on 2 LED bulbs for more than 20 h during continuous operation. Even though third LED bulb was added, the output voltage remained very stable ( $V_{\text{out}} = 2.45 \pm 0.03$  V for MFC-PVDF/AC-1 and  $V_{\text{out}} = 2.48 \pm 0.03$  V for MFC-PVDF/AC-2, respectively) regardless the fluctuation of the MFC-PVDF/ACs output currents (**Fig. 4.2a** and **4.2b**). The three LED bulbs were turned on for more than 12 days and the brightness of the LED bulbs even slightly increased (**Fig. 4.2c** and **4.2d**). When LEDs were unconnected, the output voltage increased up to  $5.20 \pm 0.57$  V for MFC-PVDF/AC-1 and  $4.35 \pm 0.32$  V for MFC-PVDF/AC-2, respectively. This result clearly demonstrates that a simple LVB is a powerful device to boost up low and unstable electrical energy harvested from domestic wastewater by a single MFC-PVDF/AC to usable levels (i.e., lighting LEDs). In this study, connecting a single LVB and a single MFC-PVDF/AC could enhance the voltage from  $< 0.4$  V to 4.35 - 5.2 V without voltage reversal. If further higher voltages are required, multiple LVB could be connected in series to a single MFC-PVDF/ACs.



**Fig 4. 2 :** (a) Time course of the Low Voltage Booster (LVB) input and output voltages and (b) LVB input current. Views of LEDs illumination powered by the boosted voltage outputs. The green arrows indicate the time period that 3 LEDs were connected. The red arrow indicates when the LEDs were unconnected (no load).



However, since the voltage reversal might occur owing to the kinetic imbalance between series-connected LVBs when a MFC-PVDF/AC supplies insufficient power to the boosters [12], MFC-PVDF/AC could be stacked in parallel in order to increase the LVB input power without voltage reversal issue. Furthermore, the LVB (consisting of a transistor, capacitors, and inductors) used in this study is easy to make and very cheap (< 1.0 US dollar) (**Table 4.1**), which is about 20-fold cheaper than the commercially available LTC 3108 DC/DC voltage regulator.

**Table 4. 1:** Estimation cost of low-cost DC-Low Voltage booster (LVB).

Item	Number	Price (¥) / unit	Price (¥)	References
capacitor	02	29	58	Aliexpress [01]
Axial Inductors	02	3	6	Aliexpress [02]
NPN transistor	01	15	15	Aliexpress [03]
Diode rectifier	01	2	2	AliExpress [04]
Total (¥)			78 (¥)	

Thus, integration of MFC-PVDF/AC and LVB is a promising approach to utilize the unusable low power energy generated by MFC. Nowadays, high step-up DC/DC converters have received considerable attention in many renewable energy system applications because renewable energy systems typically generate low voltage output [13–15]. The newly designed LVB system was found to be compatible with a low current range (0.6 - 12 mA) (**Figure 4.2b**), which are usually produced by small lab-scale MFCs. In this study, our new LVB booster system is governed by the NPN STN851 transistor. However, in case of industrial application (array of MFCs assembled in parallel), the NPN transistor-based LVB system could easily withstand a very high DC current up

to 5A (at 25 °C operating temperature) which is the absolute maximum collector current rating (IC) according to the NPN STN851 transistor manufacturer datasheet (**Table 4.2**). Furthermore, a single MFC-PVDF/AC equipped with a LVB system can drive continuously LEDs for more than 25 days whereas most of the actual commercially available or individually developed PMS failed [4,6,8]. Thus, the LVB could be a viable solution to harvest continuously the usable energy from MFC technology.

**Table 4. 2** : Operating electrical characteristic of the LVB system used in this study.  $I_{CEmax}$  is the theoretical maximum current supported by the LVB system in case of large-scale application (i.e., array of MFCs in parallel).

Symbol	Parameters	Value	Unit
$I_{CEmax}$	Current Collector-Emitter max	5	A
$I_{Bmax}$	max Base Current	1	A
$V_{CE\ max}$	Maximum Voltage Collector-emitter	60	V
$I_{EET, MFC}$	Bacterial Extracellular Electron Transfer (EET) range tested in this study to drive the LVB system	0.6-12	mA
$V_{MFC}$	MFC's working voltage range tested	0.2-0.4	V
$V_{LVB}$	Voltage LVB range obtained	2.5-5.2	V
$V_{LVB}/V_{MFC}$	DC - DC voltage gain	12.5-13	V/V
Temperature	LVB operating temperature range	15-25	°C

## **4.4 Conclusion**

In this study, we developed a Low voltage Booster (LVB) compatible with the low voltage of MFCs' technologies. Furthermore, connecting a LVB and a MFC-PVDF/AC boosted the low MFC-PVDF/AC output voltage from  $< 0.4$  V to 4.35 - 5.2 V without voltage reversal, which was sufficient enough to turn on three LED bulbs for  $> 12$  days. The integrated MFC-PVDF/AC and LVB system show excellent energy recovery regardless of the fluctuation of the input current generated by exoelectrogenic bacteria. The LVB electronic is simple, less expensive (78 (¥) /unit). .and easily scale un case of large-scale application. Also, the LVB can operate under a wide range of input current up to 5 Amperes. Therefore, the integrated MFC-PVDF/AC and LVB system could be a promising cost-effective and energy-saving domestic wastewater treatment process with renewable energy recovery.

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## **Chapter 5**

# **High voltage generation from microbial fuel cells using a newly designed low voltage booster multiplier (LVBM)**

### **5.1 Introduction**

Microbial fuel cells (MFCs) are bio-electrochemical devices that can directly convert chemical energy in biodegradable organic matter to electrical energy by exoelectrogenic bacteria as catalysis. In MFCs, exoelectrogenic bacteria extract electrons from the energy source (simply oxidation) and transfer them to the anode through diverse Extracellular Electron Transfer (EET) mechanisms (so-called anodic respiration). The resulting electrons are transported to the cathode and used for the reduction reaction of oxidized compounds (i.e., oxygen in the case of air-cathode MFC), which generates electrical power [1]. If wastewater is used as an energy source, simultaneous wastewater treatment and renewable energy production can be achieved. Therefore, it is expected that MFC technology is as a promising energy-positive wastewater treatment process and/or sustainable on-site power generation device. However, the power generated from MFCs is practically unusable (unable to directly drive even low-power electronic devices such as LEDs and wireless sensor radios) due to its high internal resistance and low voltage output, which is a current major challenge of MFC technology. The required operating voltage of such devices ranges from 2.0 V to 5 V at least and the power consumption could be up to the order of 1W [2]. The maximum

theoretical voltage across anode and cathode ( $E_{\text{cathode}}^0 - E_{\text{bioanode}}^0$ ) of a single air-cathode MFC is 1.14 V (assuming  $E_{\text{bioanode}}^0 = E_{\text{NADH}}^0 = -0.32$  V and  $E_{\text{cathode}}^0 = E_{\text{oxygen}}^0 = +0.82$  V vs. SHE at neutral pH) [3]. However, a typical observed Open Circuit Voltage (OCV) is less than 0.8 V due to the losses of the electrode potential, such as activation polarization, concentration polarization and ohmic losses [4]. The experimentally observed voltage of an air-cathode MFC is further low (0.2 to 0.5 V), which is also dependent on substrate, microorganisms, electrode overpotentials, internal resistance and applied external resistance [5,6]. Thus, the power density that an MFC can generate typically ranges from 1 mW m<sup>-2</sup> to 2000 mW m<sup>-2</sup> [4]. Thus, the MFC output voltage and power must be increased for practical uses.

To bypass the low voltage or power issue, several MFCs were simply connected in series or in parallel. However, although a serially stacked MFCs unit could provide a higher voltage, it has been proven to be difficult and ineffective due to voltage reversal (reverse polarity owing to fuel shortage) of individual MFC units, leading to a significant overall voltage decay [2,5–7].

Alternatively, a power management system (PMS) has been proposed to boost the low MFC output voltage. A PMS basically utilizes a combination of a DC/DC converter to boost low MFC voltage to usable levels and a supercapacitor to temporarily store energy. To date, various types of commercially available or individually developed PMSs were proposed to interface MFCs with electronic loads, and their performances in MFC systems were evaluated [2,6–13] (**Table 5.1**). In these studies, low MFC output voltages were increased to 2 - 12 V, which could be used to drive only low voltage electronic devices but still not enough for real-world applications. Most of the existing PMSs documented for MFC application failed to provide high step-up voltages because they are manufactured to only boost the low voltage (low input voltage limits the output voltage),

not further amplify or multiply. To further increase the voltage, a secondary voltage multiplier or amplifier of the primary boosted voltage is required.

In this study, we, therefore, propose a unique two-step “boost-and-multiply” approach, in which the low MFC output voltage is firstly boosted by a transistor-based DC/AC self-oscillating low voltage booster (LVB) circuit, and the boosted voltage was further multiplied by a multistage single-phase Cockroft-Walton voltage multiplier circuit. We have manufactured a low voltage booster multiplier (LVBM) and tested its performance using a single chamber air-cathode PVDF-based air-cathode (MFC-PVDF/AC) treating domestic wastewater as a power source [14]. A LVB with a 20-stage AC/DC multiplier circuit was able to amplify the MFC voltage (ca. 0.4 V) up to  $89 \pm 22$  V, which was the highest boosted voltage that has been ever reported, for several days without voltage reversal. The application feasibility of LVBM is discussed.

## **5.2 Materials and method**

### **5.2.1 Air-cathode MFC setup and operation**

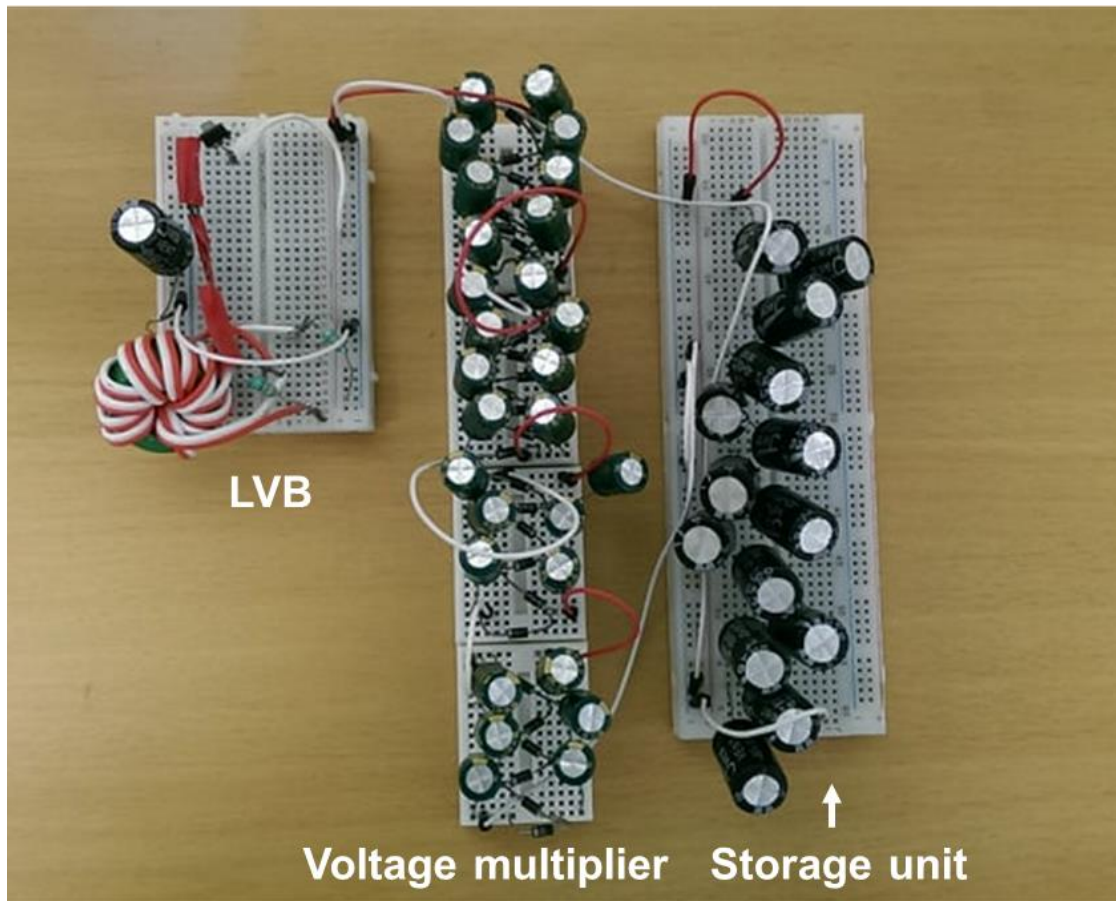
A single chamber air-cathode MFC is made from an acrylate block ( $20 \times 18 \times 3$  cm) and composed of the serpentine flow field with a working volume of 0.3 L previously described [14]. The MFC system consists of 4 anode graphite fiber brushes ( $2.2$  cm (diameter)  $\times$   $12$  cm (length), Mill-Rose, Mentor, OH) installed in 4 flow channels, which are sandwiched with 2 Separator Electrode Assembly (SEA) cells. MFC had two-sided PVDF-based activated carbon (AC) air-cathodes (thereafter MFC-PVDF/AC). The PVDF-based activated carbon (AC) air-cathodes ( $10$  cm  $\times$   $10$  cm) were fabricated by spreading 10% (w/v) PVDF solution containing  $26.5$  mg/cm<sup>2</sup> of AC (Norit<sup>®</sup> SX-Plus, Holland) and  $8.8$  mg/cm<sup>2</sup> of carbon black (CB) (Vulcan XC-72, Cabot

Corporation, USA) directly onto a stainless steel mesh (1 mm × 1 mm, type 304, Eggs<sup>®</sup>, TAIHO, Co, Japan). The MFC-PVDF/AC was inoculated with activated sludge obtained from the Sapporo Sosei wastewater treatment plant (Sapporo, Japan) and continuously fed with the primary clarifier effluent (hereafter termed as “domestic wastewater”) for more than one year (**Fig. 5.1**). After confirming that the power generation became stable, a newly designed low voltage booster multiplier (LVBM) was connected to evaluate its MFC-PVDF/AC energy harvesting performance. The MFC-PVDF/AC was operated by connecting with the LVBM that consists of different numbers of AC/DC multiplier units for 20 days and thereafter operated by disconnecting from the LVBM for 5 days. The PVDF-based activated carbon (AC) air-cathodes were chemically cleaned periodically with 1 M H<sub>3</sub>PO<sub>4</sub> to remove the inorganic chemical precipitation (e.g., NaOH) on the air side of cathodes [15].

### **5.2.2 Low Voltage Booster Multiplier (LVBM) electronic circuit**

In this study, a LVBM system was newly developed to boost and multiply the low voltage from a single MFC-PVDF/AC. The LVBM is composed of a self-oscillating LVB [14], a multistage AC/DC voltage multiplier circuit and a storage unit (**Fig. 5.1**). First, the low output DC voltage of MFC was boosted to an AC voltage via a DC/AC voltage boost converter composed of a superfast switch NPN transistor (STN851) and inductors in which energy is charged and discharged into the circuit repeatedly (**Fig. 5.2**). This repeated charge and discharge cycles of the inductors enable the transistor STN851 to turn ON and OFF the circuit at a high frequency, thus inducing a high AC voltage spike (>2 V). In this study, the transistor STN851 was selected because of its outstanding fast-switching speed and its ability to operate at a very low collector to emitter saturation voltage [16] compared to others BJTs or Metal-Oxide-Semiconductor Field-Effect Transistors (MOSFETs) commonly used as a switch.



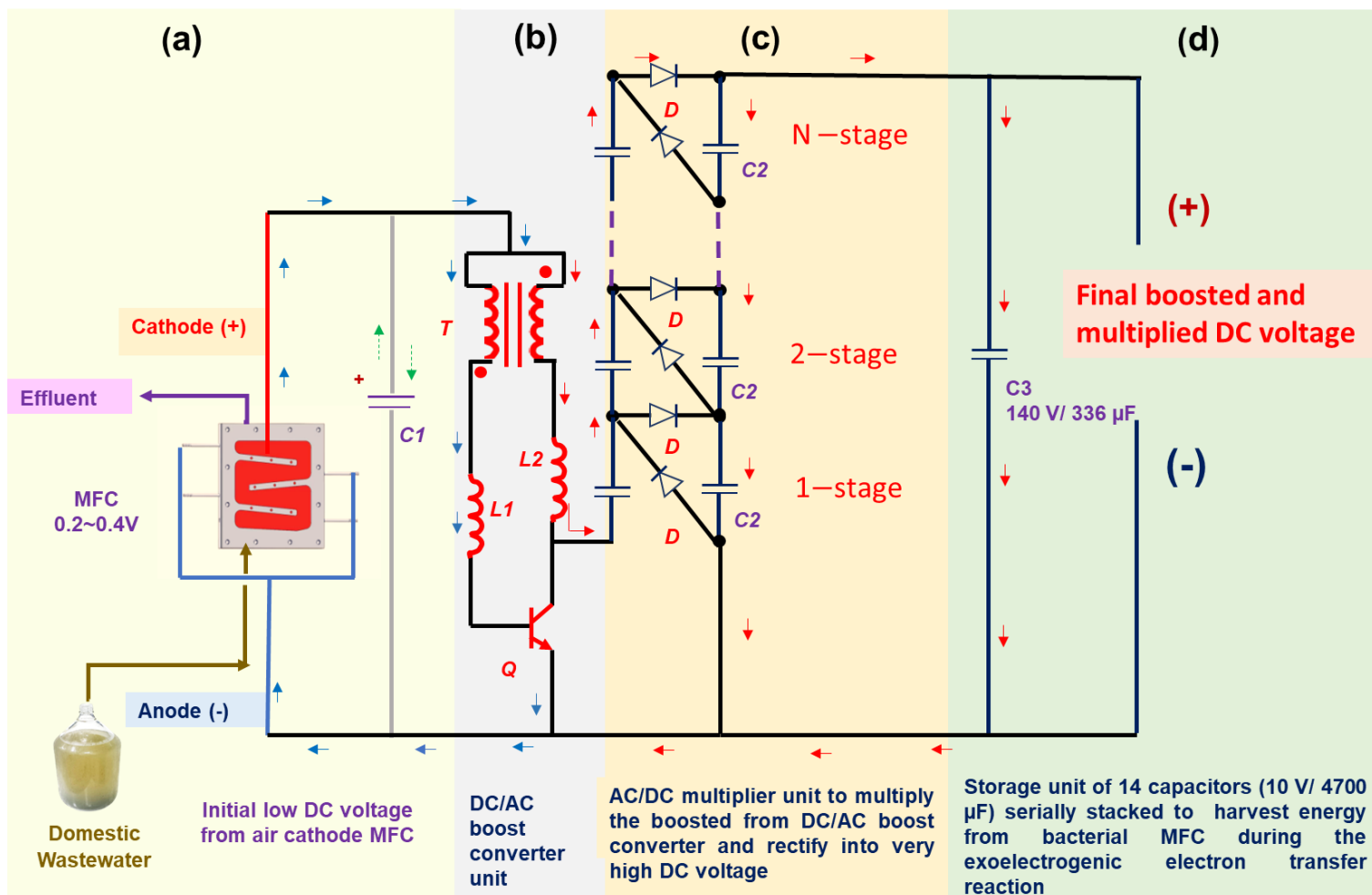


**Fig 5. 1** : Photo of the newly designed low voltage booster multiplier (LVBM) system. LVB: low voltage booster.

Second, the boosted AC voltage is multiplied and converted to a very high DC voltage output via a multistage half-wave Cockcroft-Walton voltage multiplier circuit, which is a multistage single-phase cascade circuit [17,18]. Therefore, the following voltage conversion flow is given:

Low DC output voltage of MFC  $\rightarrow$  AC boosted voltage  $\rightarrow$  Multiply AC boosted voltage  $\times N \rightarrow$   
 $\rightarrow$  the multiplied AC voltage is rectified to high DC voltage

where **N** is the number of multiplying stages (**Fig. 5.2**).

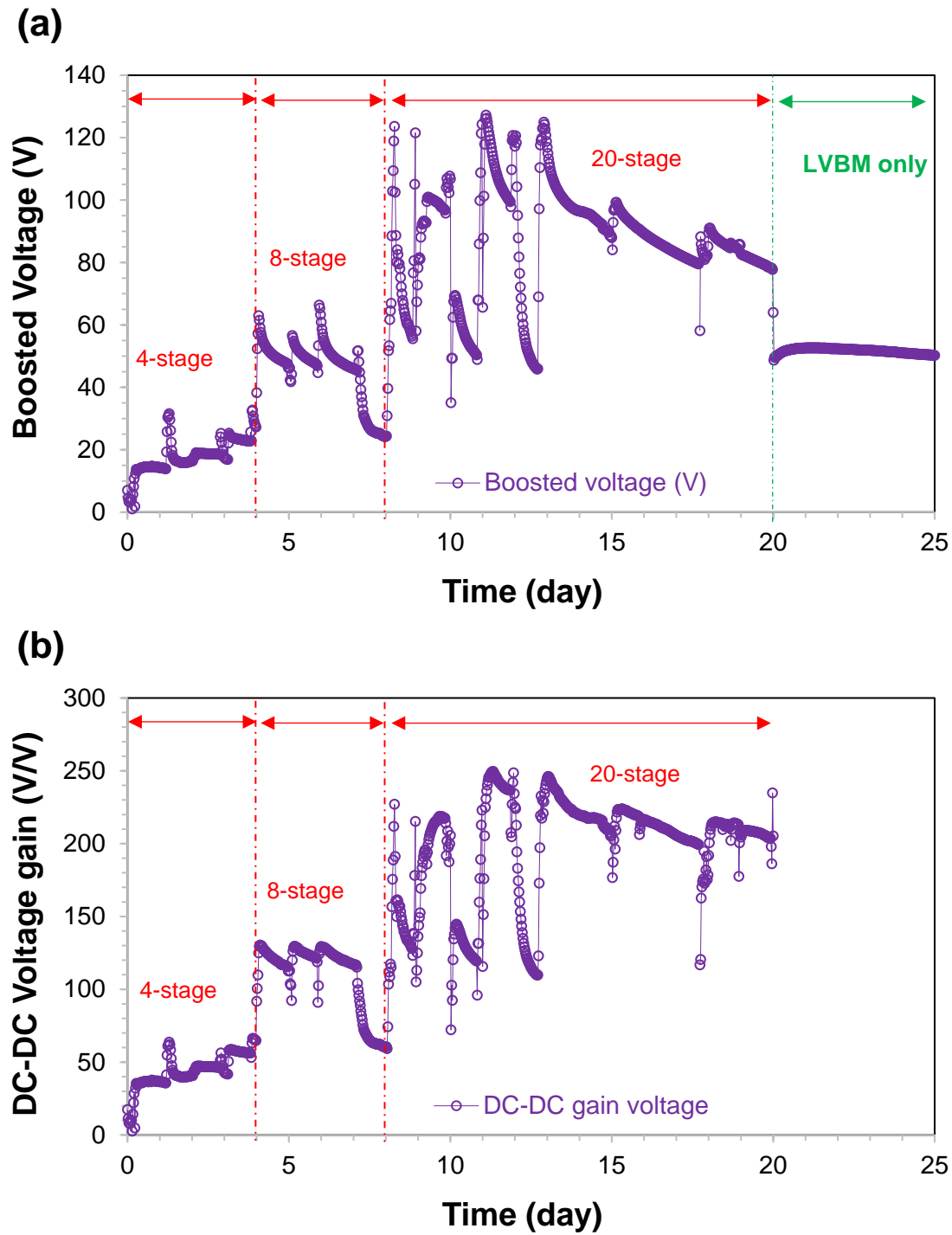


**Fig 5. 2 :** Diagram of the newly designed low voltage booster multiplier (LVBM) system connecting to a single air-cathode microbial fuel cell (MFC-PVDF/AC) which was fed with domestic wastewater as substrate. **(a)** Air cathode MFC-PVDF/AC fed with domestic wastewater, the brown and violet arrows indicate the influent and effluent, respectively. C1 is a polarized capacitor (10 V/4700  $\mu$ F) connected to the air-cathode MFC-PVDF/AC. **(b)** Self-oscillating low voltage booster electronic circuit connected to the air-cathode MFC-PVDF/AC, T is a toroid ferrite coil inductor with double windings of 20 Turns, L1 and L2 are axial inductors (680  $\mu$ H), Q is a superfast switch NPN transistor (STN851). **(c)** Half wave Cockcroft-Walton voltage multiplier circuit, C2 is a polarized capacitor (6 V/1500  $\mu$ F), D is the diode rectifier 1N4001. **(d)** Storage unit circuit, C3 is an equivalent capacitor of 14 polarized capacitors (10 V/4700  $\mu$ F) serially stacked. The blue arrows represent the conventional current flow when Q is ON, and the red arrows represent the conventional current flow when Q is OFF. The green dotted arrows represent the charge and discharge of capacitor C1.

performed every 30 minutes using a data logger (Agilent 34970A) and recorded in a personal computer. The electrode potentials were measured against an Ag/AgCl reference electrode (RE-1B,  $E_0=195$  mV vs SHE, ALS Co, Japan).

### **5.2.3 Results and discussion**

A newly designed LVBM was connected to a single air-cathode MFC-PVDF/AC and tested its performance over 25 days. The average output voltage of the MFC-PVDF/AC during the whole experimental period was  $0.43 \pm 0.04$  V. A 4-stage AC/DC voltage multiplier circuit was connected as an extension of the LVB electronic circuit (**Fig. 5.2a**) for the initial 4 days. The LVBM boosted voltage immediately increased from 2.5 V to  $18 \pm 6$  V (**Fig. 5.3a**). Connecting 8-stage AC/DC voltage multiplier circuit further increased the boosted voltage to  $46 \pm 10$  V. Furthermore, the number of multiplier circuit was increased up to 20 stages, and then the boosted voltage rapidly increased to more than 100 V (a maximum voltage of 127 V) and kept at this level for 12 days (**Fig. 5.3a**). The average voltage of  $89 \pm 22$  V was achieved, which was corresponding to about 220-fold DC to DC voltage gain (**Fig. 5.3b**). To our best knowledge, this average boosted voltage is the highest voltage ever reported for a single MFC treating domestic wastewater so far. For example, Kim et al. (2019) applied a commercially available LTC3108 voltage booster to a single air-cathode MFC fed with diluted swine wastewater ( $\sim 2$  g COD L<sup>-1</sup>) as substrate and obtained a boosted voltage of 3.3 V [6]. In addition, Park and coworkers [12] used a commercial flyback voltage booster to step up the low voltage of a single air-cathode MFC fueled with sodium acetate (2 g L<sup>-1</sup>) and obtained a boosted voltage of 5 V.



**Fig 5.3 :** (a) Boosted voltage when the air-cathode MFC-PVDF/AC is connected to the LVBM system. Red arrows indicate the boosted voltage when the LVBM with 4-stage, 8-stage and 20-stage multiplier circuits were connected, respectively. Green arrow indicates the voltage of the LVBM's output capacitors when the air cathode MFC-PVDF/AC is disconnected. (b) DC-DC voltage gain when the air cathode MFC-PVDF/AC is connected to the LVBM system.

After 20 days of operation, the LVBM was disconnected from the MFC-PVDF/AC, but the output voltage of the LVBM was held stably at  $52 \pm 0.8$  V for 5 days (**Fig. 5.3a**). This result demonstrated that since the LVBM system composed of a storage unit circuit (C3 in **Fig. 5.2d**, serially stacked 14 polarized capacitors (10 V/4700  $\mu$ F)), it could be used to store sufficient energy to power the electronic devices when the MFC-PVDF/AC voltage source is temporarily unavailable or widely fluctuated due to unstable microbial activity.

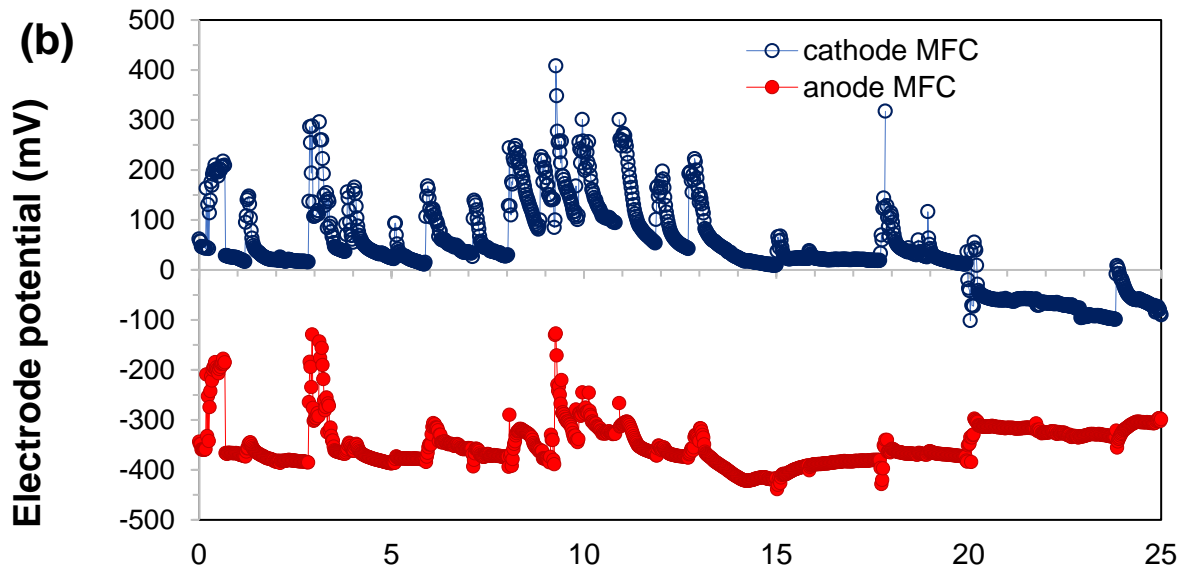
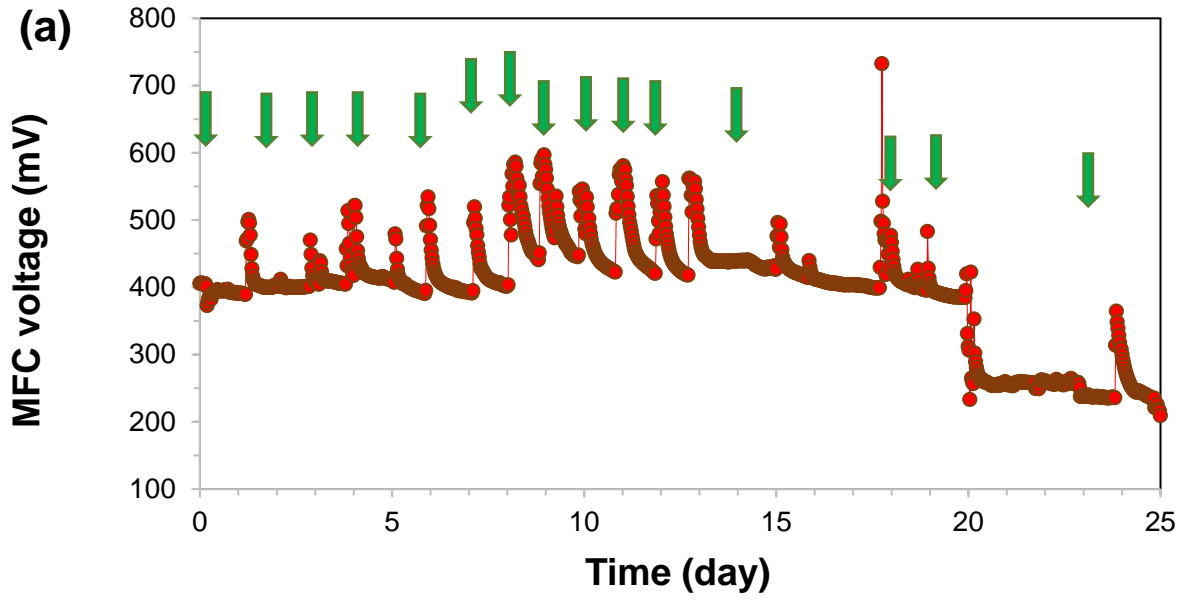
The boosted voltage fluctuated significantly during the MFC-PVDF/AC operation. This is because we periodically performed chemical cleaning of the air-cathode, which is necessary to maintain the high cathode potential (i.e., high MFC output voltage) (**Fig. 5.4a**). In fact, the MFC-PVDF/AC output voltage and current increased right after chemical cleaning, suggesting that the MFC-PVDF/AC power generation was limited by the cathodic reaction.

Power management systems (PMSs) are attracting considerable attention recently because energy harvesting or extraction technology from renewable energy sources such as MFCs produce significantly small power for practical use. It is essential to store the power and increase the output voltage when the extracted energy is used to drive any electronic devices. Various self-starting PMSs have been designed or proposed to increase the low output voltage of MFCs and tested their performance. Although some improvements have been reported, the resulting boosted voltages were able to power only low-power electronics devices such as small wireless sensors or LEDs [2,6–8,11–13,19–21] (**Table 5.1**). The highest boosted voltage reported to date was 12 V, which was harvested from a benthic MFC ( $V_{\text{MFC}} = 0.35$  to 0.5 V) using two in-line flyback converters.

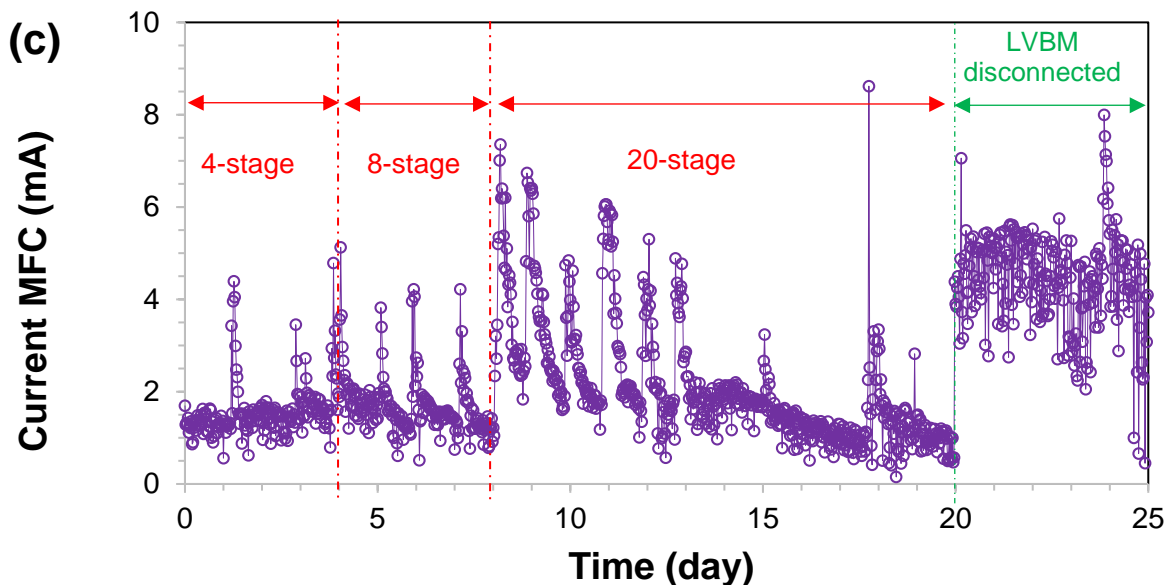
**Table 5. 1:** Comparison of previously reported MFC equipped with commercially available or individually developed power management systems (PMSs). MFC: Microbial Fuel Cell; UPEM: Ultralow Power Energy for MFC; IC: Integrated Circuit; LVBM-[n]: Low Voltage Booster Multiplier -[n] is the cascade multiplier stage number.

PMS	MFC reactor Type	MFCs	MFC working voltage	MFC-stacked configuration	Output boosted voltage	Advantage/disadvantage	References
D.C.-D.C. voltage booster circuit	Two-chamber (1.2 mL)	MFCs	0.2–0.4 V	3 MFCs unit in parallel	>3 V	Avoid voltage reversal, /low boosted voltage	[19]
Blocking oscillator booster circuit	Two-chamber (120 mL)	MFCs	0.837 V	3 MFCs unit in series	~3 V	Possible voltage reversal issue/low boosted voltage	[8]
D.C.–D.C. voltage Boost converter	Two-chamber (50 mL)	MFCs	<0.2V	Single or 4 parallel MFCs unit	3.3 V	Required very low voltage input Avoid voltage reversal/ low boosted voltage	[6]
Capacitor-based D.C.-D.C. converter	Air-cathode MFC (27 mL)		~0.5 V	4 parallel MFCs unit	2.5 V	Avoid voltage reversal/low boosted voltage	[7]
Capacitor-based D.C.-D.C. converter	Sediment Microbial Fuel Cells (550 mL anolyte, 445 mL catholyte)		0.4 V	Single MFC unit	3.3 V	Avoid voltage reversal/ low boosted voltage	[9]
Synchronous Flyback converter	Two-chamber MFCs (150 mL)		0.310 V	Single MFC unit	2.13 V	Suitable for MFC/Low boosted voltage output	[10]
Diode-based Boost converter	Two-chamber MFCs (150 mL)		0.311 V	Single MFC unit	1.83 V	Suitable for MFC/Low boosted voltage output	[10]
D.C.–D.C. voltage Boost converter+ supercapacitor	Single chamber air-cathode MFC (316 mL)		0.3 V	Single MFC unit	3.3 V	Suitable for ultralow MFC working voltage (<0.02V)/ Low voltage output.	[2]
Flyback converters	Benthic MFC		0.35–0.5 V	Large-scale benthic MFC	12 V	Easy to scale up, can be used to charge a 12-Volt	[11]

PMS	MFC reactor Type	MFC working voltage	MFC-stacked configuration	Output boosted voltage	Advantage/disadvantage	References
					battery/ relatively low boosted voltage	
Flyback converters	Air-cathode MFC (450 mL)	0.44 V	Single MFC unit	5 V	Suitable for MFC /Low boosted voltage output	[12]
Transformer-based booster+supercapacitor	Single chamber air-cathode MFC (316 mL)	0.18 V	Single MFC unit	3.3 V	Suitable for ultralow MFC working voltage (<0.02V)/ Low voltage output.	[21]
UPEM boost converter with one storage capacitor and switch IC	Sediment MFC (15 L)	0.2V	Single MFC unit	3.3 V	Suitable for ultralow current and low voltage produced by a MFC /low boosted voltage output	[13]
LVBM-[4]	Single chamber air-cathode MFC (300 mL)	0.2-0.5 V	Single MFC unit	18 V	Suitable for MFC application, can handle large variation of input current from MFC, very high boosted voltages, no voltage reversal issue, easy to implement at large-scale.	This study
LVBM-[8]	Single chamber air-cathode MFC (300 mL)	0.2-0.5 V	Single MFC unit	46 V		This study
LVBM-[20]	Single chamber air-cathode MFC (300 mL)	0.2-0.5 V	Single MFC unit	89 V		This study



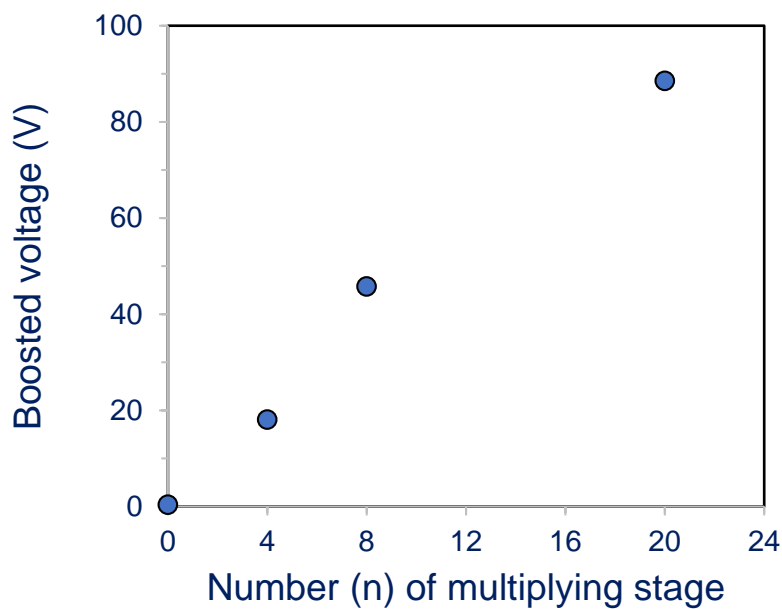




**Fig 5. 4 :** (a) Time course of the output voltage of the air cathode MFC-PVDF/AC. The green vertical arrows indicate when the air side of the cathode was chemically cleaned by 1 M of H<sub>3</sub>PO<sub>4</sub> solution. (b) Time course of the electrode potentials vs Normal Hydrogen Electrode (NHE). (c) Time course of current produced the MFC-PVDF/AC was connected to the LVBM with 4-stage, 8-stage and 20-stage multiplier circuits were connected, respectively. A green horizontal arrow indicates when the LVBM system is disconnected from the air-cathode MFC-PVDF/AC.

The newly designed LVBM in this study is based on a unique two-step approach, by which the low MFC DC voltage is boosted to AC voltage first, the AC boosted voltage is multiplied to very high DC voltage, and then the multiplied high DC voltage is stored. To our best knowledge, the boosted voltage ( $89 \pm 22$  V) in this study is the highest voltage that has been ever reported for a single air-cathode MFC treating low strength domestic wastewater (ca. 400 mg-COD L<sup>-1</sup>) so far. which was more than 220-fold DC to DC voltage gain. Moreover, the newly designed LVBM system was found to be compatible with a low current range (0.8 mA - 12 mA) (**Fig 5.4c**), which is usually produced by small lab-scale MFCs. Thus, the LVBM system enabled us to boost the low MFC-PVDF/AC voltage to the required levels without voltage reversal because only individual or parallel-connected MFCs is required to directly drive the DC/AC boost converter. In addition, since the boosted voltage is linearly correlated to the number of connected AC/DC voltage

multiplier circuits (**Fig 5.5**), we can design the LVBM which can supply high enough voltage by increasing the number of the multiplier.



**Fig 5. 5** : Correlation between the boosted voltages and the number of AC/DC voltage multiplier circuits applied. The number  $n=0$  indicates the working voltage of the single chamber air-cathode MFC-PVDF/AC.

The NPN transistor (STN851) used in the DC/AC boost converter can easily withstand high DC current up to 5A (at 25 °C operating temperature) which is the absolute maximum collector current rating (IC) (**Table 5.2**). This suggests that the NPN transistor-based LVBM system can be applied to a wide range of input current for large-scale practical MFC applications.

**Table 5. 2 :** Operating electrical characteristic of the LVBM system used in this study.  $I_{CEmax}$  is the theoretical maximum current supported by the LVBM system in case of large-scale application ( i.e array of MFCs in parallel)

Symbol	Parameters	Value	Unit
$I_{CEmax}$	Current Collector-Emitter max	5	A
$I_{Bmax}$	max Base Current	1	A
$V_{CE\ max}$	Maximum Voltage Collector-emitter	60	V
$I_{EET, MFC}$	Bacterial Extracellular Electron Transfer (EET) range tested in this study to drive the LVBM system	0.8-12	mA
$V_{MFC}$	MFC voltage range tested	0.2-0.4	V
$V_{LVBM}$	Voltage LVBM range obtained	18-127	V
$V_{LVBM}/V_{MFC}$	DC - DC voltage gain	44-250	V/V
Temperature	LVBM operating temperature range	15-25	°C

For wastewater treatment application, several MFC units must be used to obtain a higher treatment capacity and power output. However, unlike conventional fuel cells, the overall power generation performance of stacked MFCs was not stable due to unstable or uneven microbial activity, which is generally limited by the worst performing unit(s). One of the solutions could be first to connect each MFC unit with a LVBM to increase or stabilize the individual power level and then connect all MFC-LVBM units in series or parallel. This would inevitably need experimental verification.

### **5.3 Conclusion**

In this study, a low voltage booster multiplier (LVBM) was newly designed for a single air-cathode MFC-PVDF/AC and tested its performance. The LVBM system was able to increase the low MFC-PVDF/AC voltage output ( $0.43 \pm 0.04$  V) to  $88.6 \pm 22$  V and hold at this voltage level for 12 days without voltage reversal, which was more than 220-fold DC to DC voltage gain. The LVBM system was compatible with the low voltage and capable to handle widely fluctuated low current (0.8 - 12 mA) generated from low strength domestic wastewater. In addition, the LVBM output voltage was still held at  $52 \pm 0.8$  V for 5 days when disconnected from the MFC-PVDF/AC, indicating that the LVBM could be used as energy storage. Since the LVBM is relatively cheap (less than \$ 10) and easily assembled, the LVBM system is implementable as a self-starting low voltage booster or energy harvester for MFCs.

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## **Chapter 6**

# **Bioelectrochemical anodic ammonium oxidation in a single chamber Microbial Electrolysis Cell**

### **6.1 Introduction**

Microbial Electrochemical Technology such as Microbial Fuel Cell (MFC) and Microbial electrochemical Cell (MEC) has emerged as a very attractive technology for sustainable domestic wastewater treatment and bioenergy recovery. In a MFC system, exoelectrogenic bacteria oxidize organic matter and release carbon dioxide and protons into the bulk solution and electrons to the anode [1]. MECs was also used to oxidize organic matters bioelectrochemically using exoelectrogenic microbial biofilms in an anodic chamber to yield protons and electrons, which are subsequently used in a reduction reaction to produce value-added products such as hydrogen gas ( $H_2$ ) and methane gas ( $CH_4$ ) [2]. Recently, MFC technology has been used successfully in lab-scale studies to treat domestic wastewater focusing on organic matter removal and renewable energy production [3,4]. However, domestic wastewater also contains nitrogen mainly in the form of ammonium ( $NH_4^+$ ) that needs to be treated before it is discharged [3]. Usually, nitrogen in domestic wastewater is removed using biological nitrogen removal (BNR) processes consisting of aerobic nitrification and anoxic denitrification [5]. However, the BNR process is uneconomical due to the high aeration during the nitrification step and the need for exogenous organic matter in the denitrification step [5]. Ammonium-rich domestic wastewater could be treated via Anaerobic

Ammonium Oxidation (ANAMMOX) process under oxygen-limited conditions. The ANAMMOX is a biological process developed to oxidize ( $\text{NH}_4^+$ ) to nitrogen gas ( $\text{N}_2$ ) using Nitrite ( $\text{NO}_2^-$ ) as an electron acceptor. Unfortunately, ANAMMOX reaction needs  $\text{NO}_2^-$  which is very limited in domestic wastewater (<1 mg-N/L).

During this decade, ammonium removal has been widely investigated in a MEC technology [6–9]. Qu and coworkers (2013) followed by Zhan and colleagues (2014) reported anaerobic anodic ammonium oxidation process in an autotrophic MEC reactor using solid-state anode as the electron acceptor [6,7]. Furthermore, they reported that the anodic ammonium oxidation was catalyzed by *Nitrosomonas europaea*. More recently, ( in 2018) the microbe-catalyzed anodic ammonium oxidation was confirmed in an autotrophic MEC identifying *Nitrosomonas europaea* and ANAMMOX bacteria in the anodic biofilm [9]. These recent findings suggest that ammonium could be bioelectrochemically oxidized in an autotrophic MEC using solid-state anode material as an alternative electron acceptor and  $\text{NH}_4^+$  as an electron donor. Therefore, the anodic ammonium oxidation in the MEC could be a cost-effective solution avoiding the need for  $\text{O}_2$  or  $\text{NO}_2^-$  supply which is usually needed to treat ammonium-rich wastewater. To the best of our knowledge, there are few studies related to the anodic ammonium oxidation in an autotrophic MEC fed with artificial wastewater while the treatment of ammonium-rich real domestic wastewater using MEC is missing. Thus, the goal of this study is to investigate the bioelectrochemical ammonium and nitrogen removal in the single chamber MEC fed with an anaerobically pretreated domestic wastewater. MEC is microbe-catalyzed electrolysis cell, thus required an external voltage supply (>0.2 V). Here, a MEC fed with a pretreated domestic wastewater was investigated at various external applied voltages provided firstly by a MFC followed by a potentiostat.



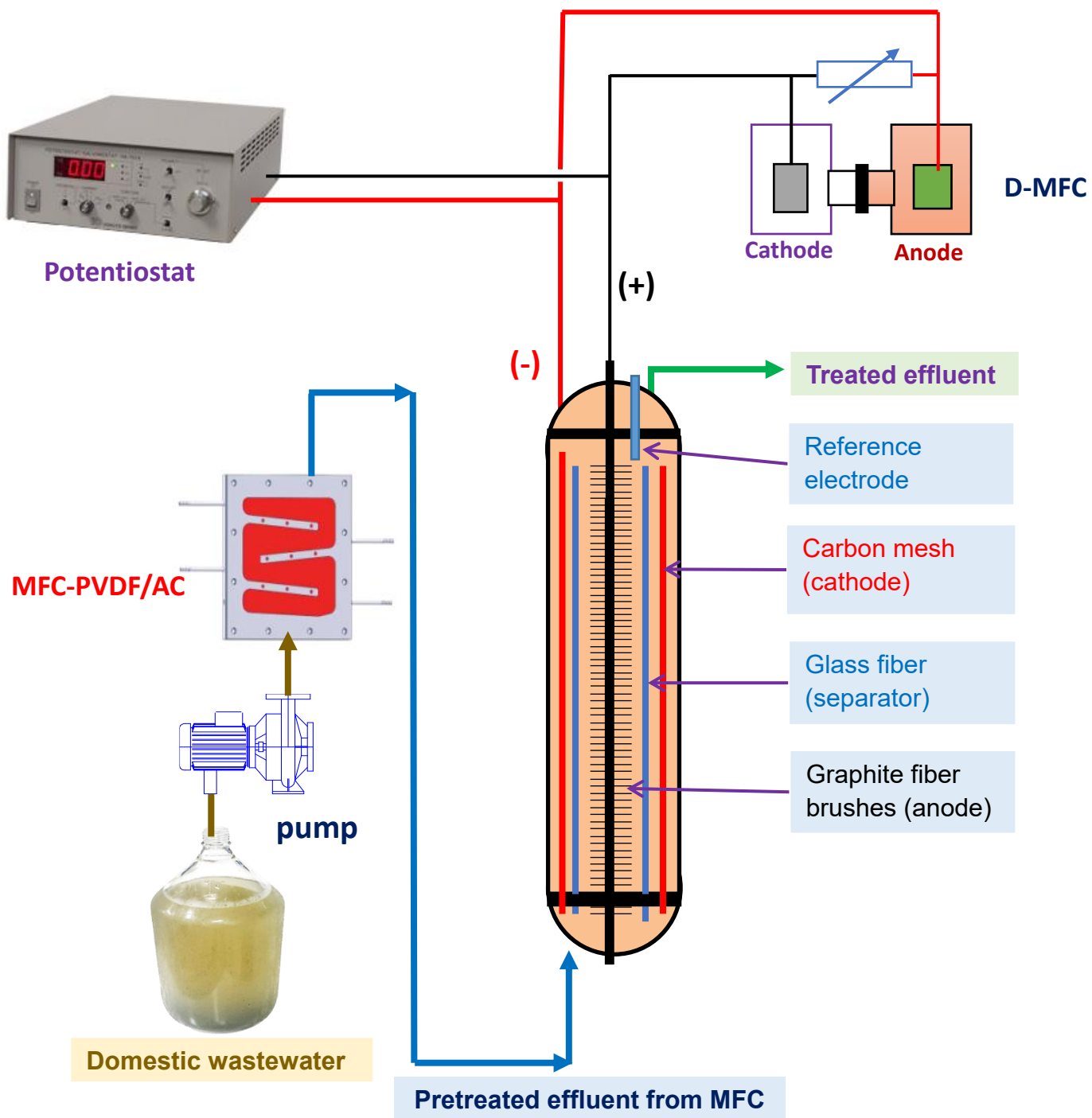
## 6.2 Materials and Methods

### 6.2.1 MEC Setup and operation

The single chamber MEC consists of 250 mL cylindric glass vessel with bottom and opening enabling the up-flow condition. The anode of the MEC was graphite fiber brush (Mill-Rose, Mentor, OH,  $\Phi \times L = 2.2 \text{ cm} \times 20 \text{ cm}$ ) and the cathode was graphite felt (Fuel Cell,  $10 \text{ cm} \times 6 \text{ cm}$ ), respectively. The graphite felt was separated from graphite fiber brush by a glass fiber (1 mm thick and  $24 \text{ mg/cm}^2$ , SAKAI SANGYO.CO., LTD, Japan,  $20 \text{ cm} \times 10 \text{ cm}$ ). used as a separator to prevent electrical short-circuit. In this study, the MEC reactor was inoculated and fed by an anaerobically pretreated ammonium-rich domestic wastewater effluent from air-cathode MFC as previously described [4] (**Fig. 6.1**). The MEC was fed and inoculate with an anaerobically pretreated domestic wastewater from MFC-PVDF/AC previously described [4]. This pretreated effluent contains COD concentration in the range of 20-80 mg/L and Total Nitrogen (TN) which is mainly in ammonium-N within the range of 20-45 mg/L (COD/TN ratio: 1 - 3).

### 6.2.2 External power supply and nitrogen measurement

In this study, the MEC was powered by a dual chamber MFC and a Potentiostat / Galvanostat (Kubota HA151B-Japan). The anode and cathode of the MFC used as an external power source were graphite felt (Fuel cell,  $4 \text{ cm} \times 4 \text{ cm}$ ), respectively. The anolyte and catholyte of the dual chamber MFC had a working volume of 250 mL, respectively separated by a Proton exchange Membrane Nafion 117<sup>®</sup>. The anolyte was fed and inoculated with effluent from a single chamber air-cathode MFC-PVDF/AC as previously described [4]. The catholyte is an abiotic chamber filled with (10 mM solution of potassium persulfate and a 0.91mg/L-phosphate buffer solution) (**Fig .6.1**).



**Fig 6.1 :** Experimental setup of the Microbial Electrolysis Cell (MEC) used as a post-treatment of a serpentine up-flow air-cathode microbial fuel cell (MFC-PVDF/AC). The double chamber MFC (D-MFC) or a potentiostat was used to power the MEC.

The effect of applied voltage value was investigated on nitrogenous compound removal rate primary in the first step (termed as step-I) via the external dual chamber MFC. Afterwards, in the second step (termed as step-II) the MFC applied as a power source was shifted by the potentiostat for other 80 days. In the Step-I, the external voltages added by the dual chamber MFC to the MEC were ~400 mV, ~500mV, ~800 mV ~1200 mV and Power Off -I, where, Power Off I denote the step-I period where the MEC was disconnected from the MFC. Afterwards, the experiment was repeated by shifting the MFC used as a power source to a more regulated power supplied via the potentiostat at the respective applied voltages of 400 mV, 800 mV, 1200 mV and Power Off -II, where Power Off II denotes the step-II period where the potentiostat was turn off. The MEC was equipped with an Ag/AgCl reference electrode (RE-1B,  $E_0=195$  mV vs SHE, ALS Co, Japan). Measurements of the current I (A) anode potential, cathode potential and added voltage (V) of MEC were performed every 30 minutes using a data logger (Agilent 34970A) and recorded in a personal computer.

The Inlet and outlet sample of the MEC were filtered through a 0.45  $\mu\text{m}$ -pore-size membrane filter (ADVANTEC<sup>®</sup>, Japan) and concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were measured using ion chromatography system IC-2010 (TOSOH; Tokyo, Japan) equipped with TSKgel IC-Anion HS or TSKgel IC-Cation HS (TOSOH; Tokyo, Japan). The Total Nitrogen (TN) was calculated as a sum of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and,  $\text{NO}_3^-$ . The experiment was conducted under continuous flow and batch test, respectively.

### 6.2.3 <sup>15</sup>N tracer experiment

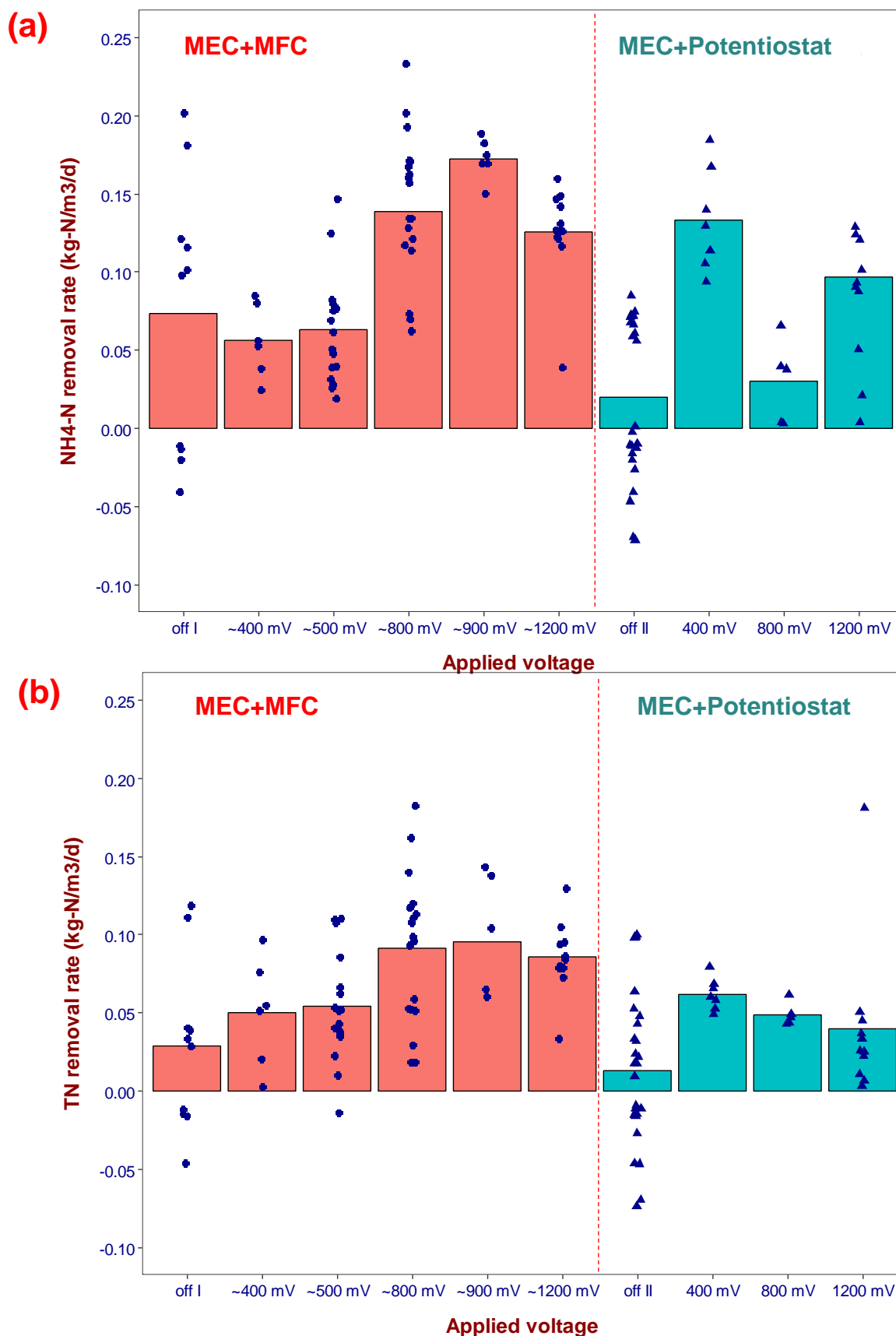
In the present study, the *ex-situ* <sup>15</sup>N tracer incubation experiment was conducted to evaluate the relative predominance and activity of ANAMMOX versus denitrifiers in the MEC. Triplicated

MEC biomass was incubated in 25 mL vial overnight at 37°C without substrate. Thereafter, the triplicated samples were amended with  $^{15}\text{NO}_2^-$  and  $^{14}\text{NH}_4^+$ . Subsequently, the accumulation of  $^{29}\text{N}_2/^{30}\text{N}_2$  was measured with gas chromatography (GCMS-QP2010 SE, Japan) under strict anaerobic condition.

## **6.3 Results and discussion**

### **6.3.1 Ammonium removal in the MEC powered by a MFC (MEC+MFC)**

After about 20-day operation, the applied voltage was consecutively changed to 900 mV, 1,200 mV, 400 mV, 500 mV, 800 mV, and to 0 mV. Average  $\text{NH}_4^+$ -N removal rates and total nitrogen removal rates under respective applied voltages were compared (**Fig. 6.2**). Even though the rates considerably fluctuated under each voltage condition due to relatively large fluctuation of the MFC output voltage, the average  $\text{NH}_4^+$ -N removal rates ( $0.061$  to  $0.173 \text{ kg-NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$ ) were dependent on the applied voltage. The higher  $\text{NH}_4^+$ -N removal rates were achieved when the voltage was set  $> 800 \text{ mV}$ . The maximum  $\text{NH}_4^+$ -N removal rate of  $0.173 \pm 0.01 \text{ kg-NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$  was achieved at 900 mV. The trend in total nitrogen removal rate was like one in the  $\text{NH}_4^+$ -N removal rates with a maximum total nitrogen removal rate of  $0.095 \pm 0.04 \text{ kg TN m}^{-3} \text{ d}^{-1}$  at 900 mV. Thus, the  $\text{NH}_4^+$ -N removal rate is higher than the previously reported values using a single chamber MEC (See **table 6.1**). For example, Zhang (2014) achieved a maximum  $\text{NH}_4^+$ -N removal rate of  $0.06 \text{ kg-NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$  with a single chamber MEC at +800 mV applied anode potential (vs. SHE) [7]. Zhang (2012) also reported higher ammonium of  $0.037 \text{ kg-NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$  when 400 mV was added to the MEC circuit (anode potential = +209 mV (vs. SHE) ) [8].



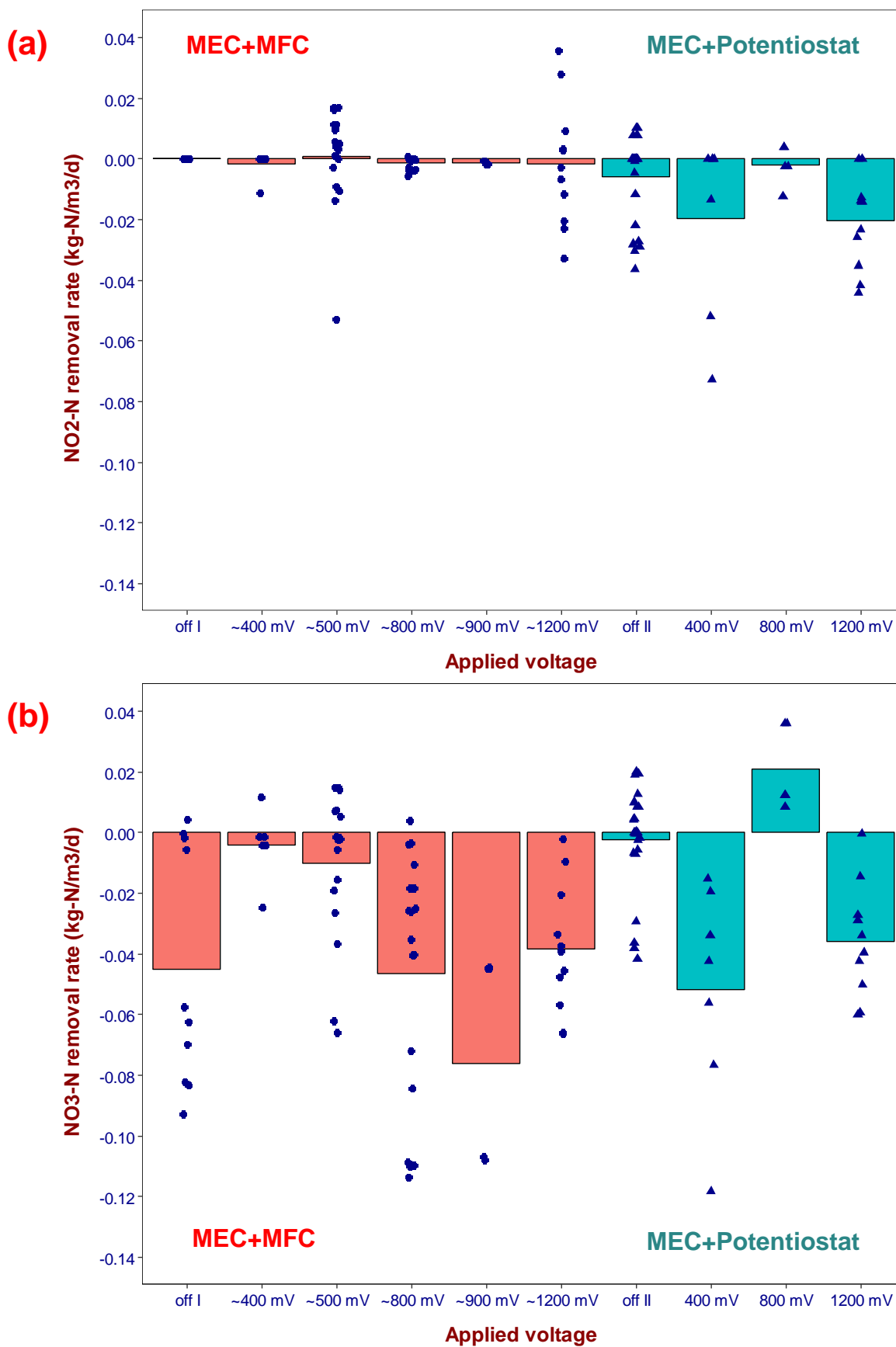
**Fig 6.2** : Comparison of (a) ammonium-N removal rate and (b) total nitrogen (TN) removal rate of MEC at various external voltages supplied. Symbols (●) and (▲) represent the data points. Bars represent the mean values. Off I and Off II: when the MEC was disconnected from MFC and the potentiostat was turn off, respectively.

Virtually, no accumulation of  $\text{NO}_2^-$  was observed during the entire operation, but  $\text{NO}_3^-$  accumulated in an applied voltage-dependent manner (**Fig. 6.3**). When the applied voltage was set  $> 800$  mV, significant  $\text{NO}_3^-$  accumulated ( $0.04 - 0.07 \text{ kg-NO}_3^- \text{-N m}^{-3} \text{ d}^{-1}$ ) (**Fig. 6.3b**). These results suggest that  $\text{NO}_3^-$  reduction was a limiting step for total nitrogen removal in this MEC.

The anode and cathode potentials ( $E^0_{anode}$  vs SHE) were directly measured under each applied voltage condition (**Fig. 6.4**). The anode potentials (vs SHE) were  $+469 \pm 147$  mV at 400 mV,  $+621 \pm 127$  mV at 500 mV,  $+677 \pm 194$  mV at 800 mV,  $+525 \pm 264$  mV at 900 mV and  $+1177 \pm 156$  mV at 1,200 mV (**Fig. 6.4a**). Accordingly, the cathode potentials ( $E^0_{cathode}$  vs SHE) became electronegative when the applied voltage was more than 500 mV with the lowest value of -300 mV at 900 mV of applied voltage (**Fig. 6.4b**).

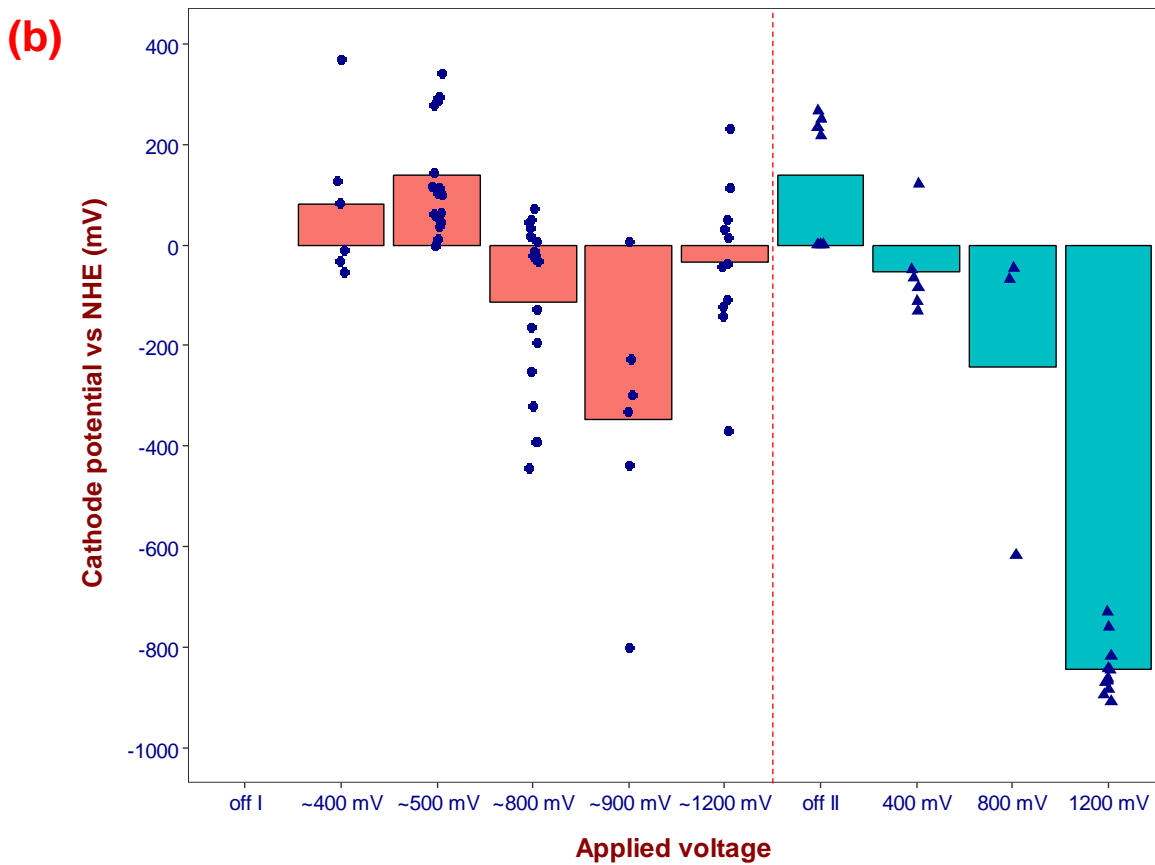
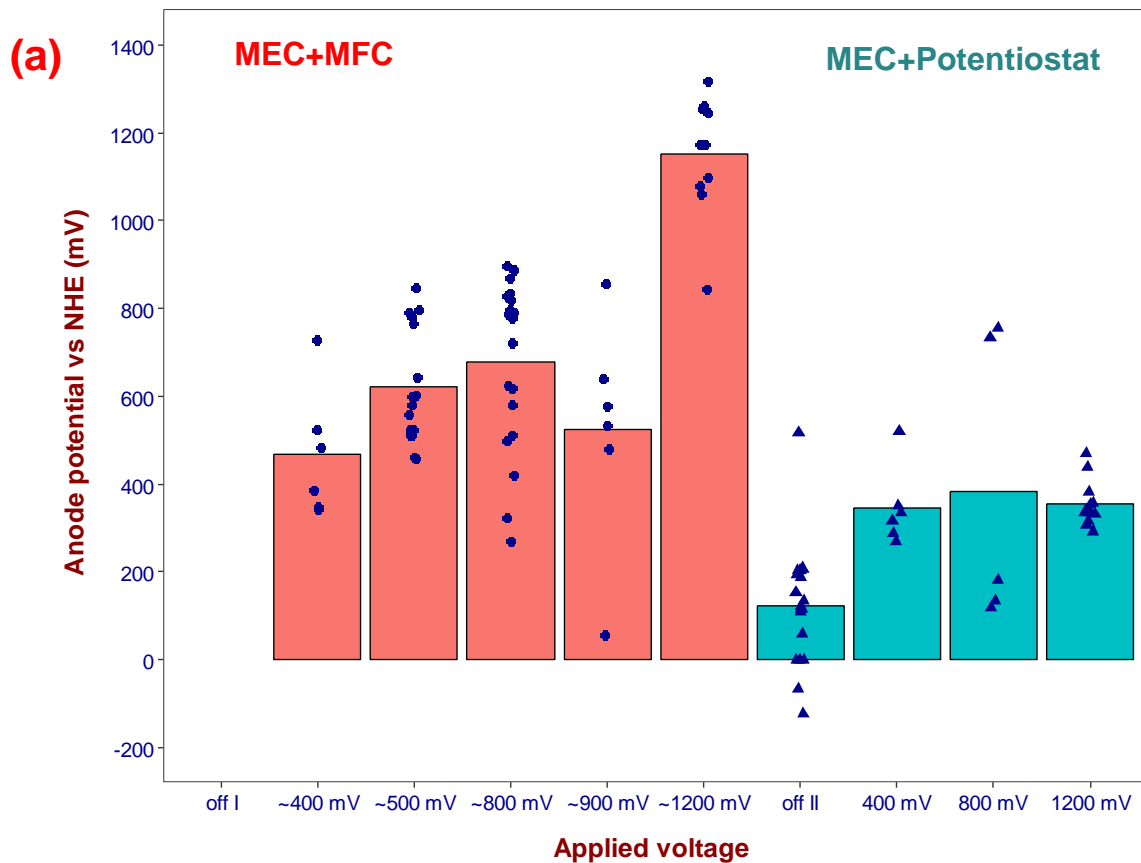
Nitrification is catalyzed step-wisely;  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$  followed by  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$ . The reduction potential of the first step of nitrification ( $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$  catalyzed by AOB),  $E_0'$  ( $\text{NH}_3/\text{NO}_2^-$ ), is  $+0.34$  V (vs SHE), and one of the second step ( $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$  catalyzed by NOB),  $E_0'$  ( $\text{NO}_2^-/\text{NO}_3^-$ ), is slightly more electropositive,  $+0.43$  V. The anode potentials under all the applied voltage conditions in the present study were more electropositive than these reduction potentials, suggesting that both the first and second step of nitrification can occur using the anode as electron acceptor in the MEC+MFC. However, in the  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$ ,  $\text{NH}_3$  is first oxidized to hydroxylamine by coupling with oxygen reduction ( $\text{NH}_3 + \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NH}_2\text{OH} + \text{H}_2\text{O}$ ) by ammonium monooxygenase (AMO), otherwise  $\text{NH}_3$  oxidation to  $\text{NH}_2\text{OH}$  ( $\text{NH}_3 + 0.5 \text{ O}_2 \rightarrow \text{NH}_2\text{OH}$ ,  $\Delta G_0' = +17 \text{ KJ mol}^{-1}$ ) is an endergonic reaction. Thus, this reaction requires two electrons and protons to reduce  $\text{O}_2$  to  $\text{H}_2\text{O}$ , and the  $E_0'$  of the  $\text{NH}_3/\text{NH}_2\text{OH}$  couple is  $+0.73\text{V}$  (vs SHE). Since some anode potentials were less electropositive than  $+0.73$  V

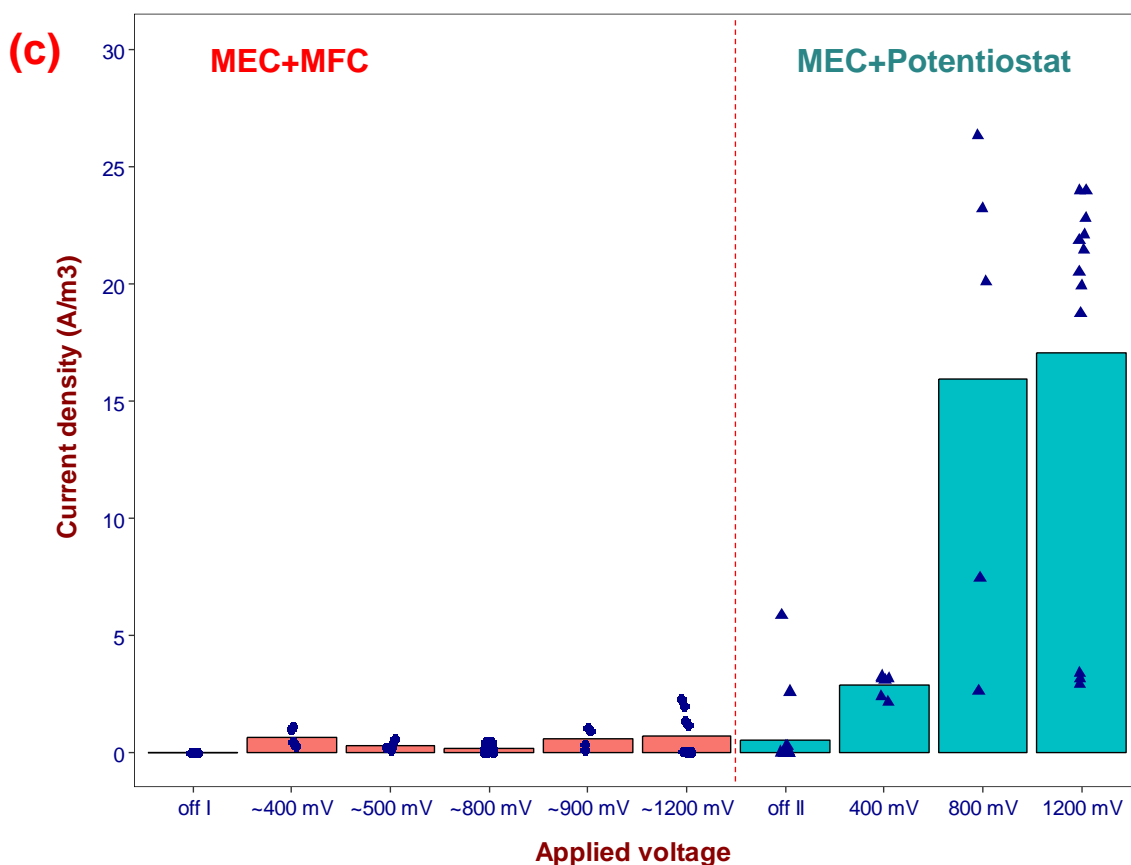
and the MEC was kept anoxic,  $\text{NH}_3$  oxidation to  $\text{NH}_2\text{OH}$  seems to be a critical step of anodic ammonium oxidation without aeration. Considering this fact, microbial anodic ammonium oxidation is theoretically possible when the anode potential is regulated above + 0.8 V (vs SHE) as previously reported [9]. Thus, minimum oxygen concentration may be required to effectively initiate the  $\text{NH}_3$  oxidation to  $\text{NH}_2\text{OH}$ , and then the oxidation of  $\text{NH}_2\text{OH}$  to  $\text{NO}_2^-$  at  $E^0_{\text{anode}} = +0.67 \pm 0.08$  V vs. SHE under controlled anode potential conditions [9].



**Fig 6.3:** Comparison of (a) NO<sub>2</sub><sup>-</sup>-N removal rate and (b) NO<sub>3</sub><sup>-</sup>-N removal rate of MEC at various external voltages supplied. Symbols (●) and (▲) represent the data points. Bars represent the mean values. Off I and Off II: when the MEC was disconnected from MFC and the potentiostat was turned off, respectively.







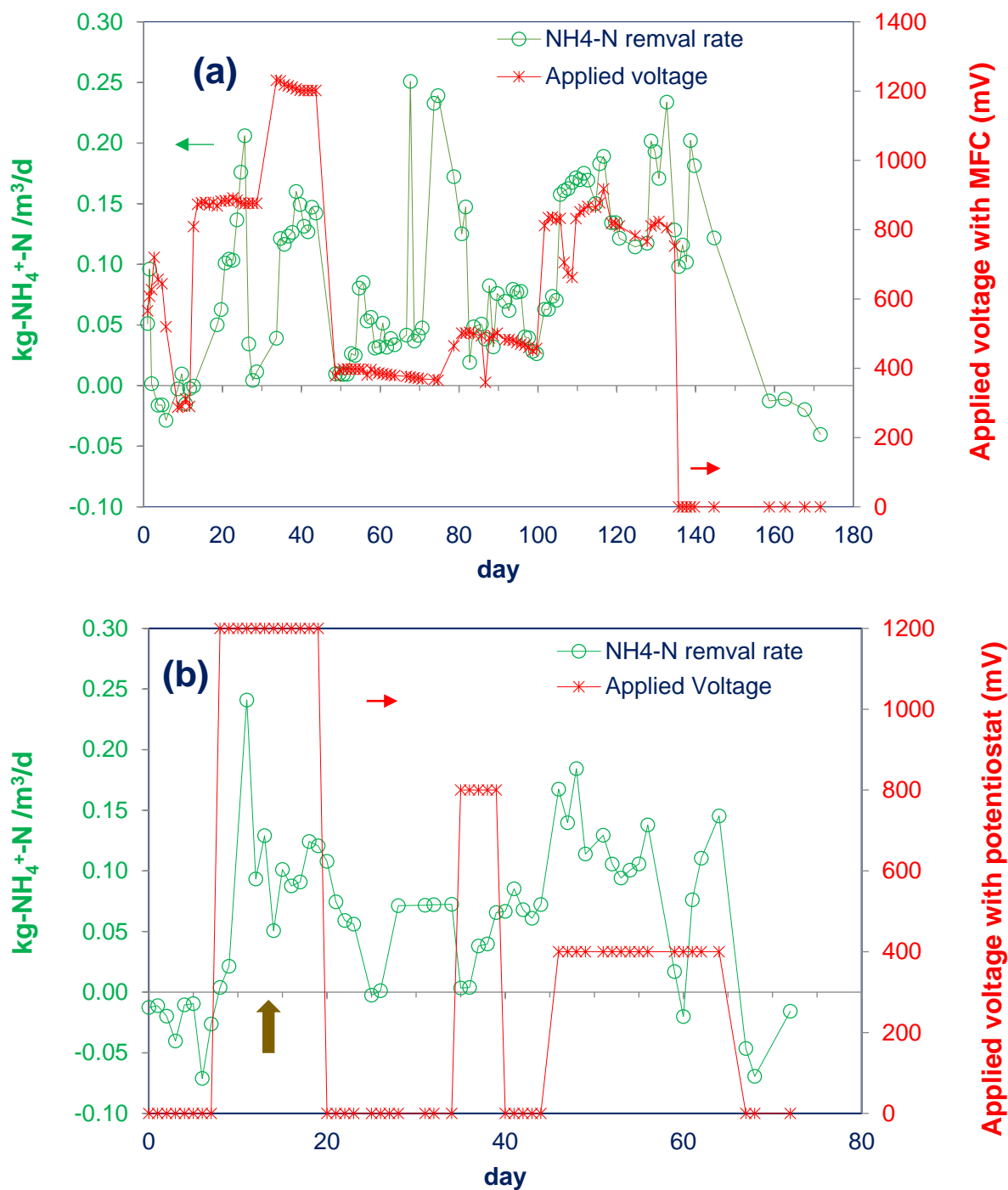
**Fig 6.4:** (a) and (b) is the respective anode and cathode potentials based on external voltages supplied, (c) Current density generated based on external voltages supplied. Symbols (●) and (▲) represent the data points. Bars represent the mean values. Off I and Off II: when the MEC was disconnected from MFC and the potentiostat was turn off, respectively.

### 6.3.2 Ammonium removal MEC powered by a potentiostat (MEC + Potentiostat)

The microbial anodic ammonium oxidation was also examined when the direct voltage was applied by a potentiostat (1,200 mV, 800 mV, and 400 mV, **Fig. 6.2**). The anode potentials ( $E^0_{anode}$  vs SHE) were  $124 \text{ mV} \pm 141$  at Off II,  $+ 347 \pm 90 \text{ mV}$  at 400 mV,  $+ 385 \pm 329 \text{ mV}$  at 800 mV, and  $+355 \pm 53 \text{ mV}$  at 1200 mV, which were slightly lower than those in the MFC+MFC (**Fig. 6.2a and Fig. 6.4a**). The cathode potentials ( $E^0_{cathode}$  vs SHE) were  $+ 224 \pm 60 \text{ mV}$  at Off II,  $- 50 \pm 90 \text{ mV}$  at 400 mV,  $-220 \pm 194 \text{ mV}$  at 800 mV, and  $-800 \pm 53 \text{ mV}$  at 1200 mV, respectively. These electronegative cathode potentials (excepted Off II) suggest that denitrification occurs easily.

The overall performance ( $\text{NH}_4^+$  oxidation and total nitrogen removal) of MEC + potentiostat was a little inferior to those of MEC + MFC. The highest  $\text{NH}_4^+$  oxidation rate ( $0.133 \pm 0.033 \text{ kg-NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$ ) and total nitrogen removal rate ( $0.062 \pm 0.01 \text{ kg-TN m}^{-3} \text{ d}^{-1}$ ) were observed at 0.4 V and slightly decreased with the increase in applied voltage from 0.4 V to 1.2 V (**Fig. 6.2a** and **6.2b**). The accumulation of both  $\text{NO}_2^-$  and  $\text{NO}_3^-$  was observed in the MEC + potentiostat (**Fig. 6.3a** and **6.3b**), indicating less nitrogen reduction by denitrifiers and/or anammox bacteria. The by-product formation of anodic ammonium oxidation (i.e., nitrate or nitrite) were dependent on the value of the applied potential, that is the anode potential (**Fig. 6.3a, 6.3b** and **6.4a**). The anode potentials in MEC + potentiostat were less electropositive ( $< 0.4 \text{ V}$ ) than those in MEC + MFC, under which  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$  was hard to occur due to  $E_0'$  of the  $\text{NO}_2^-/\text{NO}_3^-$  couple ( $+ 0.43 \text{ V}$ ). The higher anode potentials ( $> 0.5 \text{ V}$  when more than 0.8 V was applied from MFC) promoted  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$  in the MEC + MFC.

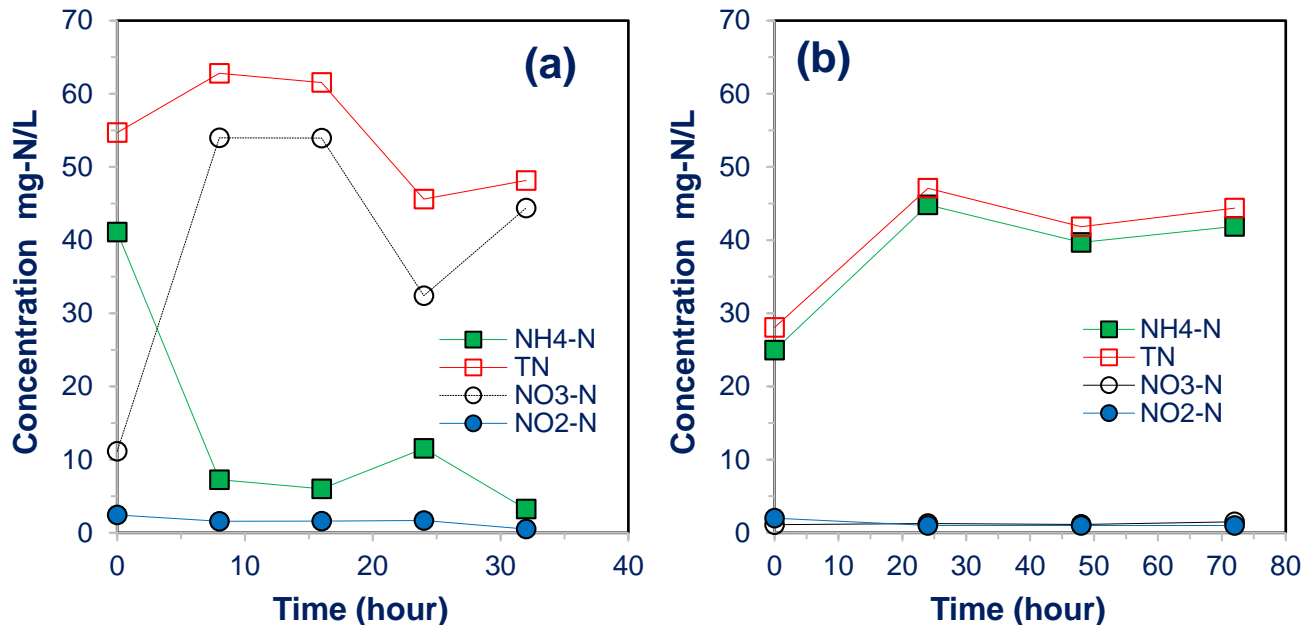
The  $\text{NH}_4^+$  oxidation coupled to total nitrogen removal was observed to a certain degree even when the power sources (both MFC and potentiostat) were disconnected from the MEC (i.e., Off I and Off II periods in **Fig. 6.2a**). The anode and cathode potentials changed slowly with time after the external power source was disconnected from the MEC. Anodic  $\text{NH}_4^+$  oxidation followed by nitrogen removal through denitrification and/or anammox continued to occur to a certain degree, which resulted in large variations of data points at Off I and Off II periods (**Fig. 6.5a & Fig. 6.5b**).

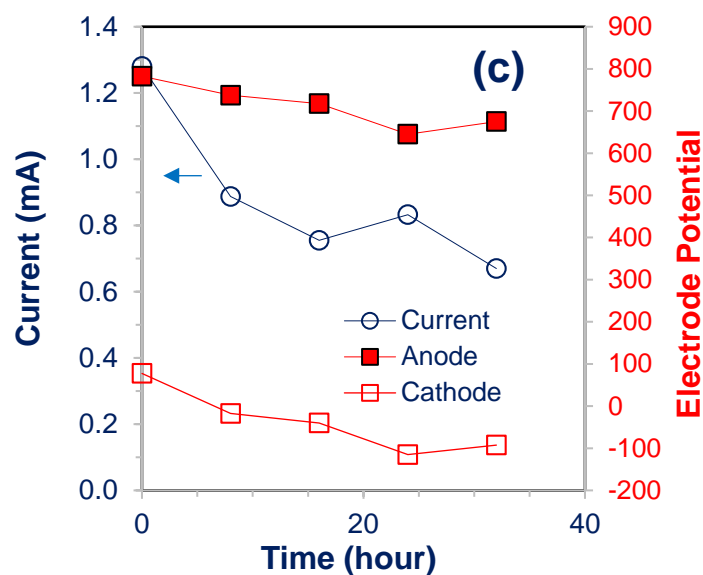


**Fig 6.5 :** Step-I (a) Applied voltage and electrodes potential at various applied voltages of MEC powered by MFC. Step-II (b) Applied voltage and electrodes potential at various applied voltages of MEC powered by the potentiostat. Brown arrow indicate when the ex situ  $^{29}\text{N}_2/^{30}\text{N}_2$  isotopic Nitrogen gas accumulation experiment was performed.

### 6.3.3 Ammonium removal in the Batch test

Batch experiments were carried out to investigate the effect of anodic respiration on the ammonium oxidation. The MEC was operated at 0.8 V supplied by a potentiostat with a closed and open external electric circuit, respectively (**Fig. 6.6a&b**). The average anode potential ( $E^0_{anode}$ ) and cathode potential were  $+712 \pm 54$  mV and  $-38 \pm 75$  mV, respectively (**Fig. 6.6c**). Approximately  $40 \text{ mg L}^{-1}$  of  $\text{NH}_4^+$  was oxidized with on significant accumulation of  $\text{NO}_3^-$  within 8 h in the closed circuit MEC, corresponding to  $0.102 \text{ kg-NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$  which is comparable with the  $\text{NH}_4^+$  oxidation rates observed in the continuous flow mode condition (**Fig. 6.2a**). In contrast, no  $\text{NH}_4^+$  oxidation occurred in the open circuit MEC (**Fig. 6.6b**). These data indicate that the  $\text{NH}_4^+$  oxidation observed in the continuous operation was mainly attributed to microbial anodic ammonium oxidation.





**Fig 6.6:** (a) Evolution of nitrogenous compounds in MEC batch experiment when 800 mV applied voltage with the potentiostat. (b) Evolution of nitrogenous compounds in MEC batch experiment when the electrical circuit of MEC was disconnected (open circuit) (c) Current generated and the electrode potentials against a reference electrode (Ag/AgCl) during the batch experiment (a).

### 6.3.4 Nitrogen removal in the MEC

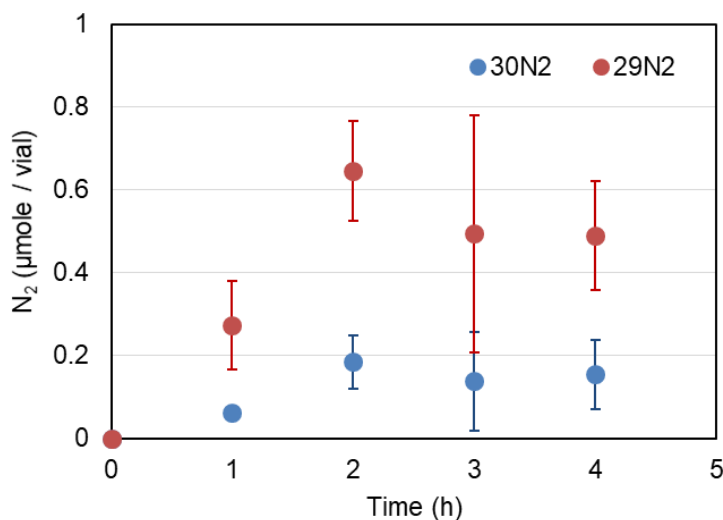
Nitrogen removal performance was evaluated at various voltages supplied by a MFC and potentiostat (**Fig 6.2b**). The average total nitrogen removal rates ( $0.07 \text{ kg-TN m}^{-3} \text{ d}^{-1}$  to  $0.09 \text{ kg-TN m}^{-3} \text{ d}^{-1}$ ) were observed when the applied voltages were set at more than 0.8 V with the MFC (**Fig. 6.2a**), which were 2 – 3 times higher than the conventional WWTPs (e.g.,  $0.035 \text{ kg-TN m}^{-3} \text{ d}^{-1}$ ) [9]. Slightly lower total nitrogen removal rates ( $0.035 - 0.05 \text{ kg-TN m}^{-3} \text{ d}^{-1}$ ) were achieved under  $> 0.4 \text{ V}$  applied voltage in the MEC + potentiostat (**Fig. 6.2b**). Under these applied voltage conditions, the cathode potentials were electronegative (**Fig .6.4b**), and oxygen was not present, suggesting that heterotrophic or hydrogen-dependent denitrification could take place. Table 6.1 reviews the comparative studies of anodic ammonium oxidation and total nitrogen removal with a MEC reactor.

**Table 6. 1** : Comparison ammonium and total Nitrogen removal in the MEC reactor.

MEC (Power source)	Substrate	Flow mode	Ammonium removal rate (kg NH <sub>4</sub> - N/m <sup>3</sup> /d)	Total Nitrogen removal rate (TN/m <sup>3</sup> /d)	Applied voltage (mV)	Anode potential E <sup>0</sup> <sub>anode</sub> (mV) vs.SHE)	References
Single chamber (MEC+Potentiostat)	SWW <sup>(A)</sup>	Batch <b>CC</b>	0.025	na	200	+209	[8]
Single chamber (MEC+Potentiostat)	SWW <sup>(A)</sup>	Batch <b>CC</b>	0.037	0.01	400	+279	[8]
Single chamber (MEC+Potentiostat)	SWW <sup>(A)</sup>	Batch <b>CC</b>	~0.06	na	na	+800	[7]
Double Chamber (MEC+Potentiostat)	SWW <sup>(A)</sup>	Batch <b>CC</b>	na	0.035	na	+800	[9]
Single chamber <b>(MEC+MFC)</b>	<b>DWW COD/N ratio 3:1</b>	Continuous flow <b>CC</b>	0.173 ± 0.01	0.095 ± 0.04	~ 900	+525 ± 264	This study
Single chamber (MEC+Potentiostat)	<b>DWW COD/N ratio 3:1</b>	Continuous flow <b>CC</b>	0.133 ± 0.033	0.062 ± 0.01	400	+347 ± 90	This study
Single chamber (MEC+Potentiostat)	<b>DWW COD/N ratio 3:1</b>	Batch and <b>CC</b>	0.102		800	+712 ± 54	This study
Single chamber (MEC+Potentiostat)	<b>DWW COD/N ratio 3:1</b>	Batch and <b>OCV (Off II)</b>	-0.02	-0.019	<b>0</b>	+124 ± 141	This study

SWW <sup>(A)</sup> : Synthetic Wastewater under autotrophic condition , **DWW** : real Domestic wastewater , **CC** : closed circuit , **OCV** : Open Circuit Condition (Off II)

Nitrogen removal (nitrate and nitrite reduction to N<sub>2</sub>) in MEC could occur via several biological routes including anammox, electrolytic autotrophic denitrification, and heterotrophic denitrification. In the present study, the nitrogen removal pathway was examined by <sup>15</sup>N tracer experiments. Independent biomass samples were taken from the top, middle and bottom of the MEC reactor (20 cm length) and incubated with <sup>15</sup>NO<sub>2</sub><sup>-</sup> and <sup>14</sup>NH<sub>4</sub><sup>+</sup> for 8 h at 37°C. The production of <sup>29</sup>N<sub>2</sub> and <sup>30</sup>N<sub>2</sub> was measured with a gas chromatograph. As a result, <sup>29</sup>N<sub>2</sub> production (<sup>14</sup>NH<sub>4</sub><sup>+</sup> + <sup>15</sup>NO<sub>2</sub><sup>-</sup> → <sup>14+15</sup>N<sub>2</sub> + 2H<sub>2</sub>O; anammox) was about three times higher than <sup>30</sup>N<sub>2</sub> production (<sup>15</sup>NO<sub>2</sub><sup>-</sup> + 3e<sup>-</sup> + 4H<sup>+</sup> → <sup>15+15</sup>N<sub>2</sub> + 2H<sub>2</sub>O; denitrification), which indicates that anammox was a dominant pathway for N<sub>2</sub> gas production in the MEC (**Fig. 6.7**). This implies that NH<sub>4</sub><sup>+</sup> is firstly oxidized to NO<sub>2</sub><sup>-</sup> with anode as an electron acceptor (anodic NH<sub>4</sub><sup>+</sup> oxidation) by AOB followed by its subsequent reduction to N<sub>2</sub> by anammox bacteria, which produce NO<sub>3</sub><sup>-</sup>.



**Fig 6.7:** <sup>29</sup>N<sub>2</sub> and <sup>30</sup>N<sub>2</sub> gas production in batch cultivation with <sup>14</sup>NH<sub>4</sub><sup>+</sup> and <sup>15</sup>NO<sub>2</sub><sup>-</sup>. <sup>29</sup>N<sub>2</sub> and <sup>30</sup>N<sub>2</sub> is produced by anammox bacteria and denitrifying bacteria, respectively. Error bar represent the standard deviation (n=3).



### 6.3.5 Microbial community analysis

To identify the microorganisms involved in the anodic ammonium oxidation and nitrogen removal in the single chamber MEC, microbial community analyses at phylum and genus levels were conducted based on the high-throughput Miseq platform and confirmed by FISH at the end of the operation. Biomass samples were collected from the graphite fiber brush anode, separator and, cathode. The results of Miseq analysis revealed a diverse community of different functional groups involved in the nitrogen cycle. The most dominant populations in the respective anode, cathode and separator attached biofilms were the phylum *Proteobacteria* (43%, 48% and 50%) followed by *Bacteroidetes* (16%, 36% and 22%), *Actinobacteria* (8%, 4%, and 11%), *Chloroflexi* (12%, 2%, and 2%), Firmicutes (6%, 4%, 6%) and *Planctomycetes* (2%, 1% and 3%) (**Table 6.2**). In terms of family-level, the microbial communities found at the anode are highly diverse where *Xanthomonadaceae* and *Sterolibacteriaceae* (8%) constitute the most abundant families followed by *Anaerolinaceae* (7%), *Chitinophagaceae* (6%), *Oxalobacteraceae* (3%), *Comamonadaceae* (3%), *Flavobacteriaceae* (3%), *Ignavibacteriaceae* (3%) and *Planctomycetaceae* (2%) (**Table 6.3**).

As for anammox bacteria, the genus *Brocadia* was detected in the anode sample (0.14%), separator sample (0.1%), and cathode sample (0.5%), respectively. Ammonium oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) such as *Nitrosomonadaceae* (0.2%) and *Nitrospiraceae* (0.2%) were also detected in the anode biofilm. *Nitrosomonas europaea* is known to oxidize ammonium anaerobically to nitrite using anode as a solid-state electron acceptor (anodic ammonium oxidation) [6,7,9,10]. The produced nitrite could be used as an electron acceptor for the oxidation of the remaining ammonium by anammox bacteria in the MEC, which thus leads to a completely non-aerated nitrogen removal process. The family *Ignavibacteriaceae* of the phylum

*Chlorobi*, which have been frequently found in electroactive-anammox reactors (electroammox) [11,12], were also detected in the anode sample (3%), separator sample (0.2%), and cathode sample (0.4%). It has been recently reported that the microorganisms in the phylum *Actinobacteria* were able to carry out anaerobic ammonium oxidation coupled to iron reduction, a process also known as Feammox [13]. Furthermore, *Acidimicrobiaceae sp.* strain A6 (A6), from the *Actinobacteria* phylum, was recently identified in a MEC as a microorganism that can carry out anaerobic ammonium oxidation using the anode as the sole electron acceptor and ammonium ( $\text{NH}_4^+$ ) as the sole electron donor [13].

This evidence might indicate that ammonium was directly oxidized to  $\text{N}_2$  with anode as an electron acceptor (electroammox) in the MEC. However, the electrogenic activity of anammox bacteria (electroammox) needs further investigations. The relatively low abundances of nitrifiers and anammox bacteria were detected in the MEC because real domestic wastewater was used as feed in the present study, resulting in the presence of high abundances of heterotrophic denitrifiers commonly found in wastewater (*Rhodoferrax*, *Dechloromonas*, *Sulfuritalea*, *Haliangium*, and *Thermomonas*).

### Summary OTU analysis table

**Table 6. 2:** Microbial community structure of the respective anode, cathode and separator biofilms at the phyla-level. The majority of dominant populations belonged to *Proteobacteria* (43 ~ 50%), In contrast, *Nitrospirae* (0.05% ~ 0.2%) and *Planctomycetes* (1% ~ 3%) are less abundant. The phylum with relative abundance which is lower than 0.03% were classified into group “Others”.

Phyla name	Abundance		
	Anode	Cathode	Separator
<i>Proteobacteria</i>	43%	48%	50%
<i>Chloroflexi</i>	12 %	2%	2%
<i>Bacteroidetes</i>	16%	36%	22%
<i>Actinobacteria</i>	8%	4%	11%
<i>Planctomycetes</i>	2%	1%	3%
<i>Nitrospirae</i>	0.2%	0.05%	0.07%
<i>Firmicutes</i>	6%	4%	6%

<i>Acidobacteria</i>	2%	0.7%	0.6
<i>Chlorobi</i>	3 %	0.7%	0.6%
<i>Chlamydiae</i>	1%	0.6%	2%
<i>Sacharribacteria_TM7</i>	2%	0.9%	2%
<i>Parcubacteria-OD1</i>	1%	1%	0.5%
<i>Gemmatimodates</i>	0.3%	0%	0.1%
<i>Hydrogendentes_NK19</i>	0.1%	0.08%	0%
<i>Peregrinibacteria</i>	0.3%	0%	0.04%
<i>Omnitrophica_OP3</i>	0.07%	0.03%	0%
<i>Caldiseria</i>	0.3%	0.2%	0%
<i>Others</i>	3%	1%	0.01%

**Table 6. 3:** Microbial community structure of the respective anode, cathode and separator biofilms at the Family-level. The majority of dominant populations of anode biofilm belonged to *Xanthomonadaceae* (8%) and *Anaerolinaceae* (7%). *Planctomycetaceae* (2%) *Ignavibacteriaceae* (3%) and *Nitrospiraceae* (0.2%) are relatively less abundant. The Family with relative abundance which is lower than 1% were classified into group “Others”.

Family name	Abundance		
	Anode	Cathode	Separator
<i>Mycobacteriaceae</i>	2%	2%	4%
<i>Nocardiaceae</i>	1%	0.4%	2%
<i>Flavobacteriaceae</i>	3%	20%	11%
<i>NVQB_f</i>	4%	0.1%	1.3%
<i>Chitinophagaceae</i>	6%	0.8%	6%
<i>Sphingobacteriaceae</i>	1%	14%	2%
<i>Parachlamydiaceae</i>	1%	0.6%	1%
<i>Ignavibacteriaceae</i>	3%	0.4%	0.2%
<i>Anaerolinaceae</i>	7%	1%	0.2%
<i>Clostridiaceae</i>	2%	2%	2%
<i>Nitrosomonadaceae</i>	0.2%	0%	0%
<i>Nitrospiraceae</i>	0.2%	0.05%	0.07%
<i>Peptostreptococcaceae</i>	2%	1%	2%
<i>Planctomycetaceae</i>	2%	1%	2%
<i>Caulobacteraceae</i>	1%	0.1%	5%
<i>Bradyrhizobiaceae</i>	2%	1%	3%
<i>Rhodobacteraceae</i>	2%	0.4%	1%
<i>Comamonadaceae</i>	3%	2%	5%
<i>Oxalobacteraceae</i>	3%	32%	3%
<i>Azonexaceae</i>	1%	0.6%	1%
<i>Sterolibacteriaceae</i>	8%	1%	1%
<i>Thiobacillaceae</i>	1%	0.4%	0.1%
<i>Polyangiaceae</i>	1%	0%	3%
<i>Moraxellaceae</i>	0.5%	0.1%	0.1%

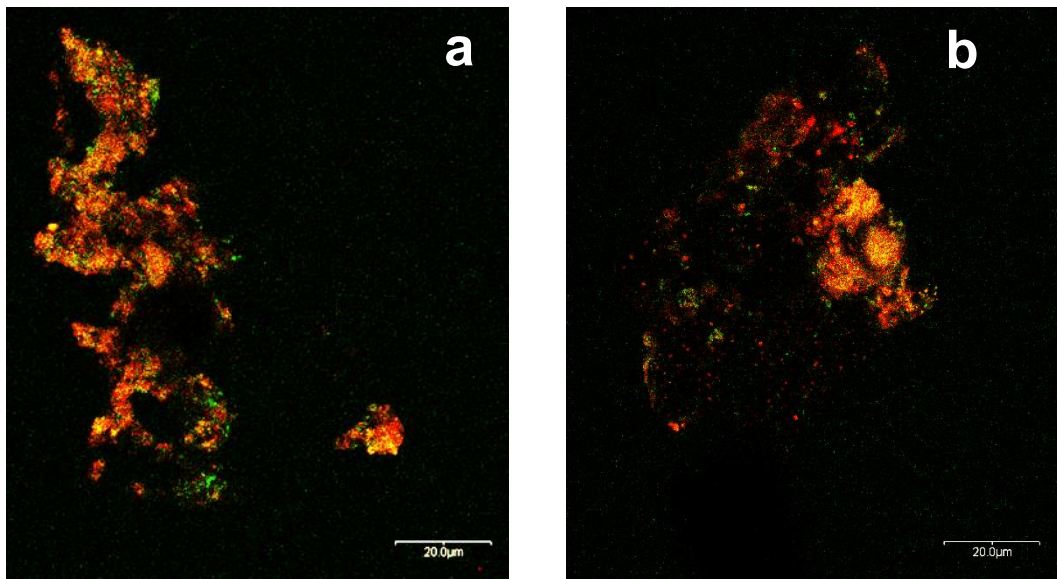
Family name	Abundance		
	Anode	Cathode	Separator
<i>Hyphomicrobiaceae</i>	0.2%	0.1%	0.6%
<i>Xanthomonadaceae</i>	8%	1%	10%
<i>Others</i>	35%	18%	34%

The distinctive microbial community was found in the cathode biofilm, which was different from ones in the anode biofilm and separator biofilm. *Janthinobacterium* within the family *Oxalobacteraceae* (32%), *Flavobacterium* within the family *Flavobacteriaceae* (20%), and *Mucilaginibacter* within the family *Sphingobacteriaceae* (14%) are three main genera in the cathode biofilm. *Janthinobacterium* has the capacity to dissimilate nitrate to dinitrogen gas and nitrous oxide (denitrification) as well as to ammonium (DNRA) [14]. *Flavobacterium* is an active member of wastewater treatment community which can carry out dissimilatory nitrate reduction to dinitrogen gas (denitrification). The members within the genus *Mucilaginibacter* have been isolated from a broad range of habitats including wastewater and produce a large amount of extracellular polymeric substance [15].

The *Planctomycetaceae* which is an ANAMMOX-related family is abundant compared to predominant majority members belonging to the families of anaerobic denitrifiers such as *Moraxellaceae* (0.5%) or *Hyphomicrobiaceae* (0.2 %). This result supports the observed result of ANAMMOX-denitrifying process take place in the MEC reactor with a high ANAMMOX contribution to remove nitrogen in the MEC reactor fed with an ammonium-rich and oxygen-limited domestic wastewater.

Fluorescence *in situ* hybridization (FISH) analysis revealed the presence of anammox bacteria in both the anode and cathode biofilms (**Fig. 6.8**). This result is in accordance with a

recently published study identifying anammox bacteria (*Brocadia*, *Kuenenia* genera) in the MEC attached biofilm [9].



**Fig 6.8:** FISH image of a cross-section of anode biofilm (a) and cathode biofilm (b) of MEC after hybridization with TRITC (red)-labeled AMX820 (specific for anammox bacteria) and alexa488 (green)-labeled EUB338, EUB338 II, and EUB338III (bacterial universal probes). The cells hybridized with both probes are shown as yellow cells. Scale represents 20 μm.

Partial anodic ammonium oxidation ( $\text{NH}_4^+ + E_{anode}^0 \rightarrow \text{NO}_2^-$ ) coupled with anammox process ( $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{NO}_3^- + \text{N}_2$ ) under anoxic condition (no aeration) with no external addition of organic carbon sources could be the main nitrogen removal route in the single chamber MEC. This promising process could save much energy by offsetting the need for aeration and nitrite supply to meet the sustainable development requirement in the field of low strength pretreated domestic wastewater.

## 6.4 Conclusion

A single chamber MEC was designed to remove ammonium nitrogen from MFC pretreated domestic wastewater without aeration. The performance of bioelectrochemical anodic ammonium oxidation and nitrogen removal was investigated at various voltages applied by a MFC and a potentiostat, respectively. The maximum ammonium oxidation rate of  $0.173 \pm 0.01 \text{ kg NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$  and total nitrogen removal rate of  $0.095 \pm 0.04 \text{ kg-TN m}^{-3} \text{ d}^{-1}$  were achieved at the applied voltage of ca. 900 mV supplied by MFC ( $E_{\text{anode}}^0 = +525 \pm 264 \text{ mV}$ ) without aeration. Similarly, the maximum anodic ammonium oxidation rate of  $0.133 \pm 0.033 \text{ kg NH}_4^+\text{-N m}^{-3} \text{ d}^{-1}$  and total nitrogen removal rate of  $0.062 \pm 0.01 \text{ kg-TN m}^{-3} \text{ d}^{-1}$  were achieved at 400 mV ( $E_{\text{anode}}^0 = +347 \pm 90 \text{ mV}$ ) supplied by a potentiostat. Furthermore, the microbial community analysis reveals the relative abundance of *Ignavibacteriaceae* and *Actinobacteria* that can carry out anaerobic ammonium oxidation using the anode as the sole electron acceptor and ammonium ( $\text{NH}_4^+$ ) as the sole electron donor (anodic respiration). These results suggest that ammonium-rich domestic wastewater could be treated “bioelectrochemically” under anaerobic condition via anodic ammonium oxidation process and aeration is not necessary for the nitrification process. Interestingly, the total nitrogen removal was accomplished via both anammox and heterotrophic denitrification in a single chamber MEC but anammox accounts for 75% of total nitrogen removal. Taken together, the anodic ammonium oxidation could be coupled with anammox and heterotrophic denitrification in a single chamber MEC, which is a cost-effective and energy-saving nitrogen removal from domestic wastewater. Finally, MFC could be used first to remove COD from wastewater, second its output voltage (0.2-0.4 V) could be used to power a MEC for the bioelectrochemical nitrogen removal.

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## Chapter 7

### Conclusion

#### 7.1 Summary of the Ph.D. dissertation

##### 7.1.1 COD and Suspended Solid removal

###### Current issues:

The Microbial Fuel Cell is considered as a promising technology due to its ability to simultaneously treat domestic wastewater and generate bioelectricity. However, its large-scale application is hindered by (i) the poor performances in terms of COD, Suspended Solid (SS), and nitrogen removal, (ii) the use of cost-prohibitive electrode (cathode), and (iii) its low voltage output ( $< 0.5V$ ) which unusable in practice.

###### Findings #1:

In this present study, simultaneous domestic wastewater treatment and renewable bioelectricity recovery were demonstrated. A serpentine up-flow Microbial Fuel Cells equipped with a low-cost polyvinylidene fluoride (PVDF)-based activated carbon (AC) air-cathode (MFC-PVDF/ACs) was tested to treat real domestic wastewater over 6- months. The MFC-PVDF/AC achieved average total COD removal rates ( $5.11 \pm 0.94$  kg-tCOD/m<sup>3</sup>/d, tCOD effluent 20-60 mg/L) and power densities ( $3.96 \pm 3.01$  W/m<sup>3</sup>) without major water leakage, which is better than those air-cathode MFCs equipped with the cost-prohibitive platinum-based air-cathode ( $5.06 \pm 0.94$  kg-tCOD/m<sup>3</sup>/d with  $1.38 \pm 0.86$  W/m<sup>3</sup>). Furthermore, the PVDF-based air-cathode is less



expensive (\$ 0.0015/cm<sup>2</sup>), more durable, robust, and easy to manufacture compared to the traditional Pt-based air-cathode (\$ 2.15/cm<sup>2</sup>). This finding suggests that PVDF-based air-cathode could be used instead of the expensive Pt-based air-cathode in case of large-scale application and could achieve excellent effluent quality.

### **Findings # 2:**

Also, the MFC-PVDF/ACs also achieved high and stable suspended solid (SS) removal efficiency (> 90% with SS effluent <20 mg SS/L) at 1.5-h HRT without any clogging event during the entire operation period, suggesting no requirement of the costly sludge treatment process. Therefore MFC-PVDF/AC could be a sustainable technology for domestic wastewater treatment to reduce the need for aeration required for the COD removal and the reduce the extra cost required for the sludge disposal.

## **7.1.2 Newly designed renewable energy harvesting system for MFC technology: (LVB and LVBM)**

### **Current issues**

Although MFC technology can produce renewable energy from the exoelectrogenic activity, the low output working voltage of a typical MFC low (0.2-0.5 V) is one of its limitations for the industrial application. To overcome this technical issue, a serially stacked MFCs unit was often proposed, However, this technical approach is limited by the voltage reversal issue which reduces the overall voltage of the serially stacked MFCs. To date, the most popular approach is to use a Power Management System (PMS) to boost up the low voltage of the MFC to a usable level (*ie.* >3 V). Unfortunately, most of the commercial or individual PMSs are not compatible with the MFC technology and required an operating voltage > 0.7 V which is higher than the working

output voltage of the MFC. Even if this is the case, the boosted voltage using the existing PMS is usually limited between 3 and 12 Volt.

**Findings #1:**

To overcome this technical issue of low voltage compatibility, a Low Voltage Booster (LVB) was specifically developed to boost the low-voltage of the MFC to a usable level. The LVB system is a self-oscillating transistor-based voltage booster developed to work under a wide window voltage ranging from 0.1 V to 30 V. In this study we demonstrated that a LVB and a MFC-PVDF/AC boosted the low MFC-PVDF/AC output voltage from  $< 0.4$  V to 4.35–5.2 V without voltage reversal, which was sufficient enough to turn on three (03) LED bulbs for  $> 12$  days. Therefore, the LVB is cheap (¥78) and could be used to harvest efficiently the usable renewable bioelectricity from the MFC-PVDF/AC.

**Findings #2:**

Furthermore, we designed and tested the new Low Voltage booster Multiplier (LVBM) dedicated to MFC fed with low strength domestic wastewater. the LVBM electronic system is a LVB connected to a AC/DC voltage multiplier circuit. This novel boost-and-multiply approach enable the LVBM to boost up the low voltage source from a single 0.3-L air-cathode MFC-PVDF/AC (0.2 - 0.4 V) to a very high DC voltage level ( $89 \pm 22$  V DC) for several days. Furthermore, the output boosted voltage is adjustable depending on the number of multiplying stages. The new LVBM system developed in this study is cheap (¥1,000), easy to assemble and scalable. To our best knowledge, this is the highest voltage generated from a single MFC that has been reported so far. The unique LVBM electronic system designed for MFC technology can support up to 5 Amperes in case of industrial application and avoid the technical issue of voltage

reversal. The MFC-PVDF/AC equipped with a LVBM electronic circuit has an excellent performance in terms of domestic wastewater treatment and usable high voltage generation (>80 V) suggesting that the combined MFC-PVDF/AC + LVBM could be used as a cost- and energy-saving primary wastewater treatment system.

### **7.1.3 Microbe-assisted anodic ammonium oxidation in a Microbial Electrolysis Cell Technology.**

#### **Current issue**

Biological Nitrogen Removal (BNR) is widely used as the main process used to treat ammonium-rich wastewater by aerobic nitrification followed by anodic denitrification. Unfortunately, this process expensive (need for aeration and exogenous carbon supply). The alternative and cost-effective process to remove ammonium from wastewater via the anodic ammonium oxidation process using an autotrophic Microbial Electrolysis Cell fed with synthetic wastewater was recently initiated. However, the anodic ammonium oxidation data using real domestic wastewater is missing.

#### **Findings**

In this study, the performances of the microbe-assisted anodic ammonium oxidation and nitrogen removal were investigated at various voltages applied by a MFC and a potentiostat, respectively. This study reveals that ammonium could be oxidized via microbe-assisted anodic ammonium oxidation. Anodic ammonium oxidation reaction (anodic respiration) was achieved when the MEC is powered by a MFC or a potentiostat. Therefore, the MFC could be a cost-effective external power source to the MEC for nitrogen removal. Furthermore, bacteria belonging to the families of *Ignavibacteriaceae* and *Actinobacteria* that can carry out anaerobic ammonium using the anode as the sole electron acceptor and ammonium as the sole electron donor (anodic

respiration) were detected in the anodic biofilm. These results suggest that ammonium-rich domestic wastewater could be treated bioelectrochemically under anaerobic condition via anodic ammonium oxidation process and aeration is not necessary for the nitrification process. Also, the bioelectrochemical anodic nitrification could be couple with a biological anammox process for nitrogen removal. These findings suggest that nitrogen removal in domestic wastewater could be achieved by a sustainable and cost-effective anodic ammonium oxidation followed by a biological anammox and denitrification for nitrogen removal.

## 7.2 Conclusion

Taken all these findings together, we can conclude that, a MFC-PVDF/AC with a LVBM circuit has an excellent performance of domestic wastewater treatment and usable high boosted voltage suggesting that it could be used as a cost- and energy-saving primary wastewater treatment system. The integrated system (MFC-PVDF/AC) + MEC+LVBM could be used to as a sustainable bioelectrochemical removal of COD, SS, and nitrogen in domestic wastewater, thus offsetting the need of aeration and can recover valuation renewable energy in the same time.

## 7.3 Recommendations for a pilot-scale application

In the case of pilot-scale configuration, we recommend to electrically connect all the individual MFC-PVDF /AC unit in parallel to a LVBM to harvest more electrical current during the domestic wastewater treatment. If one pilot-scale MFC-PVDF/AC produces in average 50 mA, the maximum number of parallely connected MFC-PVDF/ACs to a LVBM system could be:

$$N_{\text{MFCs,parallel}} = \frac{I_{\text{LVBM,MAX}}}{I_{\text{MFC,pilot}}} = \frac{5000 \text{ mA}}{50 \text{ mA}} = 100 \text{ MFC-PVDF/ACs (working volume of 100 Liters),}$$

where  $I_{LVBM,max}$  is the maximum input current of the LVBM = 5 000 mA = 5 A.

Also, the boosted voltage ( $V_{LVBM}$ ) when a MFC-PVDF/AC connected to a LVBM depends to the number of multiplying stages and the electrical current from bacterial Extracellular Electron Transfer process ( $I_{EET, MFC}$ ). The experimental studies revealed that the lab-scale (0.3Liter) MFC-PVDF/AC and a LVB connected with 20-stages voltage multiplier (*ie* LVBM-20) generated a constant  $V_{LVBM} > 100$  V when the  $I_{EET, MFC} > 5$  mA. Based on these experimental data, the valuable energy recovery assuming 24 hours of operations for a single pilot-scale MFC-PVDF/AC unit could be:

$$E_{recovery} = 0.05A \times (V_{LVBM}) \times 24 \text{ hours} = 0.05A \times 100 \text{ V} \times 24 = 120 \text{ Wh} = 0.12 \text{ kWh.}$$

Where  $V_{LVBM} = 100$  V.

From these assumptions, a single pilot-scale could recover 0.12 kWh of renewable energy during the treatment of 0.1 m<sup>3</sup> of domestic wastewater (assuming HRT =24 hours) Therefore, Net energy recovery using one pilot-scale MFC-PVDF/AC equipped with a LVBM system could be:

$$\text{Net Energy Recovery (NER)} = \frac{0.12 \text{ kWh}}{0.1 \text{ m}^3} = 1.2 \text{ kWh/ m}^3 \text{ corresponding to the theoretical}$$

internal energy from raw the domestic wastewater treatment (see Chapter 1- introduction). Therefore MFC-PVDF/ACs equipped with LVBM could be an attractive approach for domestic wastewater treatment and energy recovery at a pilot-scale. Also, the pilot-scale MEC applied for ammonium removal and H<sub>2</sub> production need further researches. Finally, the integrated pilot-scale (MFC-PVDF/AC), LVBM, and MEC could be a promising self-powering system for simultaneous domestic wastewater treatment and harvesting renewable electricity and required more investigations and financial support.

