

## Improving the dynamic response of a mediator-less microbial fuel cell as a biochemical oxygen demand (BOD) sensor

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### Abstract

The dynamic behavior of a mediator-less, microbial fuel cell (MFC) was studied as a continuous biochemical oxygen demand (BOD) sensor. The response time and the sensitivity were analyzed through the step-change testing of the fuel concentration. The MFC of 25 ml had the shortest response time of  $36 \pm 2$  min at the fuel-feeding rate of  $0.53 \text{ ml min}^{-1}$  and the resistance of  $10 \Omega$ . A smaller MFC of 5 ml had a response time of  $5 \pm 1$  min.

### Introduction

A microbial fuel cell (MFC) is a device that can directly convert chemical energy of organic or inorganic fuel into electricity. It can be operated without mediators using an electrochemically active, metal-reducing bacterium, such as *Shewanella putrefaciens* (Kim *et al.* 1999a, b, 2002) or a microbial consortium (Kim *et al.* 2004). The mediator-less MFC was studied for the development of a biochemical oxygen demand (BOD) sensor (Gil *et al.* 2003, Kang *et al.* 2003, B.H. Kim *et al.* 2003, M. Kim *et al.* 2003, Chang *et al.* 2004a, b, Moon *et al.* 2004). The MFC-type BOD sensor is a promising alternative BOD sensor for on-line measurements and has an operational stability of over 5 years with good agreement between  $\text{BOD}_5$  determined by conventional means (B.H. Kim *et al.* 2003; M. Kim *et al.* 2003).

Recently, an MFC was used to monitor BOD continuously (Chang *et al.* 2004a) and good correlation was observed between the BOD values and the steady-state current output from the MFC. It took about 60 min to reach a new steady-state current after MFC had been fed with different

strengths of wastewaters. A response time of 60 min though is too long. A BOD sensor has been reported with the measuring time less than 10 min including recovery time (Liu & Mattiasson 2002). To improve the performance of an MFC as a novel BOD sensor in terms of the response time, the dynamic behavior of the MFC and its possible contributions to the response of current output should be identified and analyzed.

In this work, a transient response in an MFC for the continuous monitoring of BOD is analyzed and optimized. Studies were made to identify the effect of the fuel-feeding rate and the resistance of the external load on the response time and sensitivity. Based on the results suggestions are made for a rational strategy to improve dynamic response of the MFC.

### Materials and methods

#### *Microbial fuel cells (MFC)*

MFCs were constructed using transparent polyacrylic plastic, which consisted of the anode and

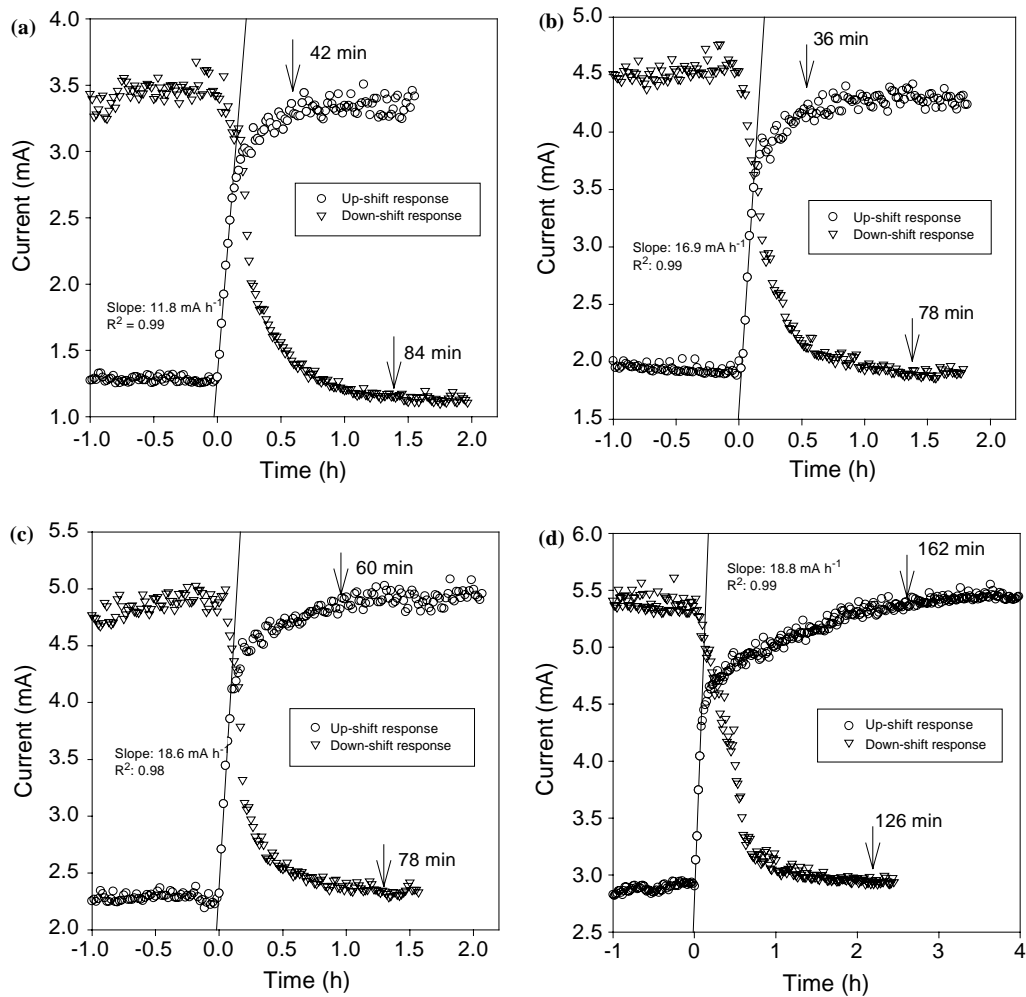


Fig. 1. Effects of fuel-feeding rate on the current generation during step-wise changes in fuel concentration from 50 to 100 mg BOD l<sup>-1</sup> (up-shift) and from 100 to 50 mg BOD l<sup>-1</sup> (down-shift). (a) 0.35 ml min<sup>-1</sup>, (b) 0.53 ml min<sup>-1</sup>, (c) 0.65 ml min<sup>-1</sup>, (d) 1 ml min<sup>-1</sup>. The resistance was 10  $\Omega$ . Each average response time ( $n = 3$ ) was indicated by arrow. The response time was defined arbitrarily as the time to reach 95% of the new steady-state current.

cathode compartments separated by a cation exchange membrane (Nafion 450, DuPont Co., Wilmington, DE, USA). Each compartment was 25 ml (void vol.: 20 ml) or with the anode volume of 5 ml (void vol.: 4 ml). Electrochemically active microorganisms were enriched within the MFC and maintained for over 2 years (Chang *et al.* 2004a). The potential between anode and cathode was measured using a multimeter (Model 2700, Keithley Instruments, Inc., Cleveland, OH, USA) linked to a differential multiplexer (Model 7701, Keithley). Data were recorded digitally on a personal computer *via* an IEEE-488 interface card

(Model PCI-488, Keithley) every 60 s. The measured potential was converted to current according to the relationship of potential = current  $\times$  resistance.

#### Fuel

Artificial waste-water (AW) containing glucose and glutamic acid was used as throughout the study (Chang *et al.* 2004a). For step-change testing, AW with 50 or 100 mg BOD l<sup>-1</sup> was used. The other details of the AW preparation have been described previously (Chang *et al.* 2004a).

### Continuous operation and step response testing

The AW was fed through the injection port of the anode compartment at a rate of  $0.35 \sim 1 \text{ ml min}^{-1}$  ( $57 \sim 20 \text{ min}$  as HRT) using a peristaltic pump equipped with Marprene II tubing. Air-saturated tap water was fed to the cathode compartment as oxidant at the feeding rate of  $9.5 \text{ ml min}^{-1}$  throughout the study using a peristaltic pump. The MFC was controlled at  $33 \text{ }^\circ\text{C}$ . The current generation patterns were analyzed with the step changes in fuel feeding speed either in up-shift mode from  $50$  to  $100 \text{ mg BOD l}^{-1}$  or in down-shift mode from  $100$  to  $50 \text{ mg BOD l}^{-1}$ . All experiments were conducted three times at least, and the typical results or mean values were presented.

## Results and discussion

### Effect of fuel-feeding rate on step change response

The response time, arbitrarily defined as the time required to reach 95% of the new steady-state current, was determined after the fuel concentrations were changed in up-shift and down-shift modes at different feeding rates. As shown in Figure 1, at all fuel-feeding rates, except at  $1 \text{ ml min}^{-1}$ , the responses to the up-shift were slightly faster than those to the down-shift. When the fuel concentration was increased at a low fuel feeding rate, the response time was shorter than the HRT, which is believed to be due to the reduced void volume resulting from microbial growth and to the non-ideal flow in the anode compartment. The fastest response was determined to be at the feeding rate of  $0.53 \text{ ml min}^{-1}$  in both shifts.

The current increased in two distinct phases of initial fast response, followed by a slow increase when the fuel concentration was increased. At the higher feeding rate the difference was more significant. Due to this difference, the shortest response time under the up-shift conditions was shown at an intermediate feeding rate of  $0.53 \text{ ml min}^{-1}$ . The fast current increase in the first phase might be related to the forced transport of fuel by feeding, which determined the overall response at the fuel-feeding rates of lower than  $0.53 \text{ ml min}^{-1}$ . On the other hand, at higher feeding rates it seems that the overall response is

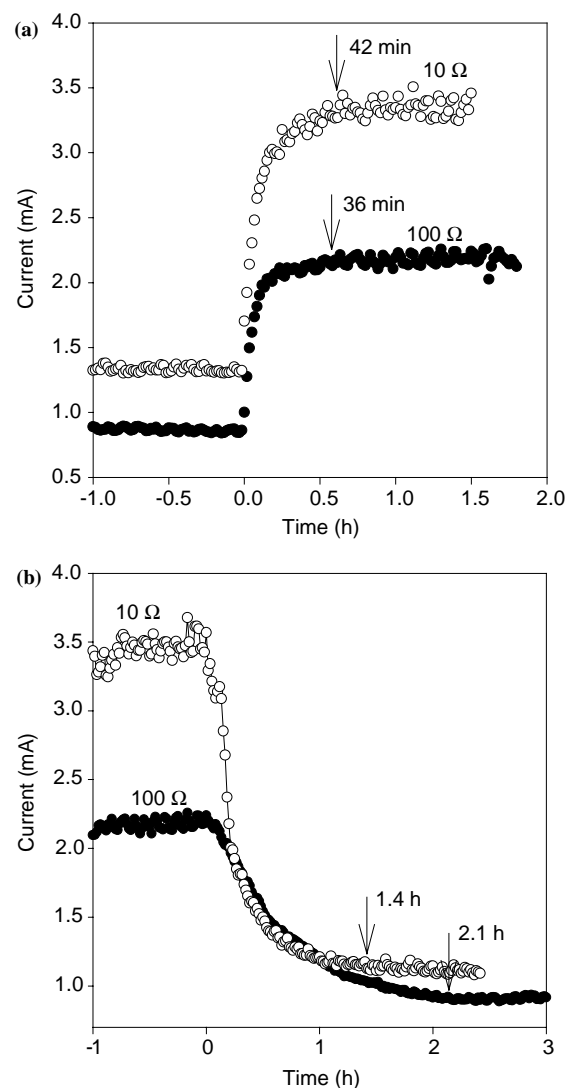


Fig. 2. Effects of resistance on current response to step-wise changes in fuel concentration. (a) Up-shift, (b) down-shift. The fuel-feeding rate was  $0.35 \text{ ml min}^{-1}$ . The arrows indicate average response time ( $n = 3$ ).

governed by dispersion or diffusion processes of fuel, probably due to non-ideal fuel flow.

The highest sensitivity of  $0.053 \text{ mA (mg l}^{-1}\text{)}^{-1}$  was observed at the fuel-feeding rate of  $0.65 \text{ ml min}^{-1}$ ; only slightly higher than at  $0.53 \text{ ml min}^{-1}$ . The feeding rate of  $0.53 \text{ ml min}^{-1}$  has been determined to be the optimal fuel-feeding rate for the  $25 \text{ ml}$  MFC, since this rate resulted in the shortest response time without compromising the sensitivity.

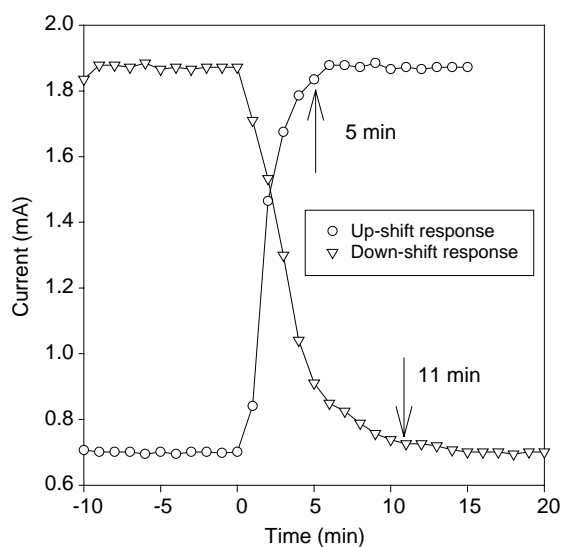


Fig. 3. The current generation during step-wise changes in fuel concentration from 50 to 100 mg BOD l<sup>-1</sup> (up-shift) and from 100 to 50 mg BOD l<sup>-1</sup> (down-shift) using MFC with reduced cell volume. The volume of the anode compartment and the electrode area were 5 ml and 8 cm<sup>2</sup>, respectively. The fuel-feeding rate was 0.53 ml min<sup>-1</sup>. The resistance was 10 Ω. Each average response time ( $n = 3$ ) was indicated by arrow. The response time was defined arbitrarily as the time to reach 95% of the new steady-state current.

#### Effect of resistance on step change response

The MFCs were operated at the resistance of 10 or 100 Ω to determine the effects of resistance on the response. As shown in Figure 2, when an MFC was run at the fuel-feeding rate of 0.35 ml min<sup>-1</sup> with a resistance of 100 Ω, the response time was 36 ± 1 min; slightly shorter than that of 10 Ω in the up-shift. However in the down-shift, the response time was 126 ± 5 min with 100 Ω; considerably longer than that of 10 Ω. These results show that the resistance limits the current at the up-shift mode to reach the maximum value. They are consistent with the previous results (Gil *et al.* 2003). When fuel was fed at 0.35 ml min<sup>-1</sup>, the sensitivity was 0.026 mA (mg l<sup>-1</sup>)<sup>-1</sup> with 100 Ω resistance, which is about 60% of that with 10 Ω. From these results, the resistance of 10 Ω was selected among the tested resistances, to operate the MFC as a BOD sensor.

#### Dynamics of MFC and its design

A rational strategy to reduce the response time can be formulated through the analysis of the

dynamic characteristics of the MFC. Assuming that the MFC is a plug-flow reactor and other dynamics such as microbial and electrochemical effects are negligible within a certain range of fuel concentration, current will respond linearly after changes in fuel concentration. Consequently, the new steady-state can be attained exactly at HRT, through manipulation of the fuel-feeding rate. Diminishing the HRT can give a shorter response time at a fixed cell void volume. The previous results showed that the response time could not be further reduced in the flow rates of over 0.53 ml min<sup>-1</sup> using a 25 ml anode volume MFC, due to tailing problems at high fuel-feeding rates.

A new C-type MFC was designed with the cell volume of 5 ml (void vol.: 4 ml). The geometric design of the C-type MFC structure is similar to that of the S-type MFC used above, with a difference of reduced height. The C-type MFC was operated with the step-change of fuel concentration from 50 to 100 mg BOD l<sup>-1</sup> and 100 to 50 mg BOD l<sup>-1</sup> at the fuel-feeding rate of 0.53 ml min<sup>-1</sup> (HRT: 7.5 min). As shown in Figure 3, the response times for up-shift change and down-shift change could be reduced to 5 ± 1 and 11 ± 2 min, respectively. Tailing problems in the current signal were not observed. It shows that scaling down an MFC can reduce the non-ideal flow. The linear range of the calibration curve was from 20 to 200 mg BOD l<sup>-1</sup> (data not shown) and was comparable to that using the previous MFC (Chang *et al.* 2004a).

**In conclusion**, the current generated from an MFC continuously fed with fuel in step-changes of concentration, was analyzed to understand and optimize the reactor as a BOD sensor. The dynamic performance of an MFC was affected not only by the HRT, but also by external resistance. Through the analysis of the dynamic characteristics of MFCs, a newly designed MFC with the reduced anode volume of 5 ml decreased the response time from 36 ± 2 to 5 ± 1 min.

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