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Supporting information

Enhancement of the sensitivity of microbial fuel cell sensor by transient-state

operation

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Fig. S1. The polarization curves and power density curves of four MFC sensors. Two of them were with the transient-state mode in the following tests, while the remaining two were used as the control.



Fig. S2. The performance of the MFC sensor operated with an open circuit as a control when fed acetate from 0 to 10 mM. (B) The relationship between the voltage output and the acetate concentration.



Fig. S3. The MFC sensor equivalent circuit model. It consisted of two internal resistors (Ohmic resistance, R_o and activate resistance, R_{ct}) and one internal capacitor (C_{in}). Within each cycle, the U_{MFC} can be divide into U_{on} when the MFC sensor was connected to the external resistance, and the U_{off} when the MFC sensor was disconnected to the external resistance.

Based on the equations of 1-5, the first derivative of U_{off} with respect to the R_{ct} and the

 $C_{\rm in}$, are respectively as following:

$$\frac{dU_{\rm off}}{dR_{\rm ct}} = \frac{dU_{\rm on}}{dR_{\rm ct}} e^{\frac{-t_{\rm off}}{\tau}} + (U_{\rm on} - U_{\rm oc}) e^{\frac{-t_{\rm off}}{\tau}} \frac{(R_{\rm o} + R_{\rm ext})^2 C_{\rm in}}{(R_{\rm o} + R_{\rm ct} + R_{\rm ext})^2}$$
(S1)

$$\frac{dU_{\rm off}}{dC_{\rm in}} = \frac{dU_{\rm on}}{dC_{\rm in}} e^{\frac{-t_{\rm off}}{\tau}} + (U_{\rm on} - U_{\rm oc}) e^{\frac{-t_{\rm off}}{\tau}} \frac{R_{\rm ct}(R_{\rm o} + R_{\rm ext})}{(R_{\rm o} + R_{\rm ct} + R_{\rm ext})}$$
(S2)

The first derivative of V_{on} with respect to the R_{ct} and the C_{in} , respectively as following:

$$\frac{dU_{\rm on}}{dR_{\rm et}} = -\frac{U_{\rm oc}R_{\rm ext}}{(R_{\rm o} + R_{\rm et} + R_{\rm ext})^2} + \left(\frac{dU_{\rm off}}{dR_{\rm et}} + \frac{U_{\rm oc}R_{\rm ext}}{(R_{\rm o} + R_{\rm et} + R_{\rm ext})^2}\right)e^{\frac{-t_{\rm os}}{r}} + \left(U_{\rm off} - U_{\rm oc}\frac{R_{\rm ext}}{R_{\rm o} + R_{\rm et} + R_{\rm ext}}\right)e^{\frac{-t_{\rm os}}{r}} \frac{(R_{\rm o} + R_{\rm ext})^2C_{\rm in}}{(R_{\rm o} + R_{\rm et} + R_{\rm ext})^2}$$
(S3)

$$\frac{dU_{\rm on}}{dC_{\rm in}} = \frac{dU_{\rm off}}{dC_{\rm in}} e^{\frac{-t_{on}}{\tau}} + (U_{\rm off} - U_{\rm oc} \frac{R_{\rm ext}}{(R_o + R_{\rm ct} + R_{\rm ext})}) e^{\frac{-t_{\rm on}}{\tau}} \frac{R_{\rm ct}(R_o + R_{\rm ext})}{(R_o + R_{\rm ct} + R_{\rm ext})}$$
(S4)

The first derivative of the con-MFC sensor output voltage U_{co} with respect to the R_{ct} and the C_{in} , are respectively as following:

$$\frac{dU_{\rm co}}{dR_{ct}} = -\frac{U_{\rm oc}R_{\rm ext}}{\left(R_o + R_{\rm ct} + R_{\rm ext}\right)^2} \tag{S5}$$

$$\frac{dU_{\rm co}}{dC_{\rm in}} = 0 \tag{S6}$$

Before the exposure of toxicity, that is the initial state, the tra-MFC sensor and the con-MFC sensor were all expected to hold similar basic parameters as evidenced by the polarization curves and power density curves (Fig. S1). The basic parameters in the initial state are listed as follows:

$$C_{\text{in}}=0.01, R_{\text{O}}=400 \Omega, R_{\text{ct}}=100 \Omega, R_{\text{ext}}=330 \Omega, U_{\text{on}}=0.12 \text{ V}, U_{\text{off}}=0.4 \text{ V}, U_{oc}=0.6 \text{ V}$$

Among these basic parameters, the C_{in} was estimated based on the study by Fradler et al. [1], where the same anode material was used. The total internal resistance of 500 Ω calculated from the power density curves was used to calculate the R_{ct} by separating it from the solution resistance, R_{O} . The R_{ext} was fixed in the study, while the U_{on} , U_{off} , and U_{oc} were all measured at the initial state.

By putting the basic parameters into the formula (S1-S6), the absolute value of the first derivative of U_{off} of the tra-MFC sensor was dramatically larger than that of both the U_{on} of the tra-MFC and voltage of the con-MFC sensor, with respect to both the R_{ct} and the C_{in} . It can be concluded that the output signal of U_{off} , when the MFC sensor was disconnected to the external resistance, was the best option to improve the sensitivity for toxicity monitoring.

References

[1] Fradler KR, Kim JR, Boghani HC, Dinsdale RM, Guwy AJ, Premier GC. The effect of internal capacitance on power quality and energy efficiency in a tubular microbial fuel cell. Process Biochem. 2014;49:973-80.