Modelling of a CH_4-producing microbial electrosynthesis system for energy recovery and wastewater treatment

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Section 1: experimental operation of CH_4-producing MESs

A glass bottle with 350 mL was used as the bioreactor for a single-chamber MES, and two carbon clothes (12 cm^2, TMIL Ltd., Ibaraki, Japan) were used as the anode and cathode, respectively. The distance between the anode and cathode was 2 cm, and the electrodes were connected to a power source (Array 3645 A, Array Electronics, Nanjing, China) by titanium wires. To cultivate the MES, the effluent (100 mL) from a CH_4-producing MES operated for 6 months and medium (150 mL) were added into the reactor, and the output voltage of the power source was set at 0.82 V. The medium mainly contained 15 mmol L^{-1} acetate, 50 mmol L^{-1} PBS (19 mmol L^{-1} KH_2PO_3, 31 mmol L^{-1} Na_2HPO_3) and other microelements [1]. Before operation, the reactor was flushed by pure N_2 to remove oxygen. The solution in reactor was exchanged by fresh medium when the current density decreased to 0.5 A m^{-2}. The gaseous and liquid products were analyzed per day by a gas chromatography and an ion chromatography, respectively according to our previous studies [1-3]. The pH of solution was detected using a pH-meter (PHS-2F, INESA scientific instrument Co., Ltd, Shanghai, China) by extracting 1 mL of the electrolyte from the reactor per day.

Section 2: operation and electron transfer of a CH_4-producing MES

A voltage of 0.7 ~ 1.0 V is usually applied to a CH_4-producing MES. Fig. S1 shows the variation of the current and electrode potential of a MES operated under 0.7 V. As shown in this figure, the cathode potential is kept at ~ −1.15 V *vs.* Ag/AgCl during the stable operation of the MES, indicating that the cathode potential is always lower than −1.0 V *vs.* Ag/AgCl during the operation of MESs under typical applied voltages. In this condition, electrons are mainly transferred from cathode surfaces to cathode biofilms through the indirect electron transfer pathway [2].

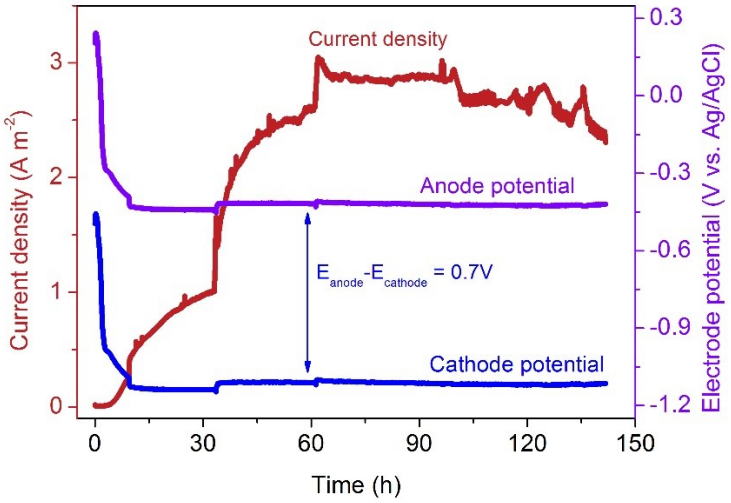

Fig. S1 Variation of the current and electrode potential of a CH_4-producing MES operated under 0.7 V

Section 3: kinetics of biocathodes

As shown in Fig. S2, when the biocathode operated at the potential higher than −0.8 V vs. Ag/AgCl, nearly no current was generated on it. When it operated at the potential lower than −0.8 V vs. Ag/AgCl, the generated current was mainly contributed to indirect electron transfer, indicating that H_2 was first generated on the biocathode, and then H_2 was further conversed to CH_4 in biofilms or bulk solution [1, 2]. In this case, we used a piecewise function to describe the kinetics current generation with −0.8 V vs. Ag/AgCl as the critical point.

Furthermore, as the conversion of H_2 to CH_4 ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) was not an electrochemical reaction and methane was the main products observed in our experiments, thus we assumed the conversion of H_2 to CH_4 as a non-limiting step. Therefore, we only considered the electrochemical kinetics of hydrogen generation using the Bulter-Volmer-Monod equation.

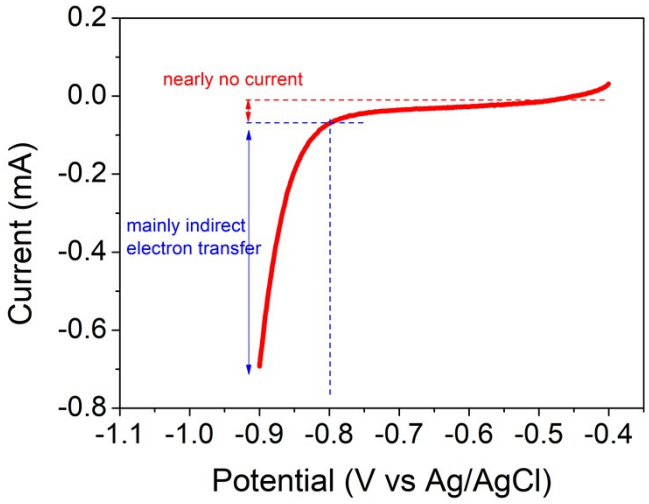

Fig. S2 Current generation of the biocathode under different potentials.

Section 4: equation construction of pH factor

The original equations used to illustrate the influence of pH on bioanode activities was illustrated as Eq. S1 [4]:

$$r_{ut} = \begin{cases} 0, & pH < pH_{opt} - W \\ \frac{\hat{q}X_f}{2}\left(1 + \cos\left(\frac{\pi}{W}(pH - pH_{opt})\right)\right), & pH_{opt} - W < pH < pH_{opt} \\ \hat{q}X_f, & pH > pH_{opt} \end{cases} (S1)$$

where, r_{ut} indicated the rate of substrate utilization, $\hat{q}X_f$ indicated the maximum rate of substrate utilization in the biofilm, W indicated a parameter for pH inhibition, and pH_{opt} indicated the optimum pH for anode biofilm.

As the microorganism activity was proportional to the substrate utilization rate which was proportional to the current density generated by bioelectrodes, we defined **pH factor** (dimensionless) as the value of r_{ut} divided by $\hat{q}X_f$, thus the pH factor of bioanodes was shown as Eq. S2:

$$\alpha_{pH,a} = \begin{cases} 0, & pH < pH_{opt,a} - W_a \\ \frac{1 + \cos\left(\frac{\pi}{W_a} \cdot (pH - pH_{opt,a})\right)}{2}, & pH_{opt,a} - W_a \le pH \le pH_{opt,a} \\ 1, & pH > pH_{opt,a} \end{cases} (S2)$$

To construct the equation of cathode pH factor, we first experimentally tested the variation of biocathode current under different pH [5]. Then, we modified Eq. S2 according to our experimental data and constructed Eq. S3.

$$\alpha_{pH,c} = \begin{cases} \frac{1 + \cos\left(\frac{\pi}{W_c} \cdot (pH - pH_{opt,c})\right)}{2}, & pH_{opt,c} - W_c \le pH \le pH_{opt,c} + W_c \\ 0, & pH < pH_{opt,c} - W_c \; or \; pH > pH_{opt,c} + W_c \end{cases} (S3)$$

Section 5: illustrations of D_i^{eff} and S_i

Table S1. Illustrations of the efficient diffusion coefficient and bioelectrochemical source item of species *i*

Species *i*	S_i	D_i^{eff}		Value of S_i in biofilms	
		In biofilm	In diffusion layer	Anode biofilm	Cathode biofilm
$CO_2(aq)$	$S_{CO_2(aq)}$	$\epsilon_p^{1.5} D_{CO_2(aq)}$	$D_{CO_2(aq)}$	0	0
HCO_3^-	$S_{HCO_3^-}$	$\epsilon_p^{1.5} D_{HCO_3^-}$	$D_{HCO_3^-}$	0	0
CO_3^{2-}	$S_{CO_3^{2-}}$	$\epsilon_p^{1.5} D_{CO_3^{2-}}$	$D_{CO_3^{2-}}$	0	0
OH^-	S_{OH^-}	$\epsilon_p^{1.5} D_{OH^-}$	D_{OH^-}	0	$\frac{i_c}{2FL_{B,c}}$
H^+	S_{H^+}	$\epsilon_p^{1.5} D_{H^+}$	D_{H^+}	$\frac{7i_a}{8FL_{B,a}}$	0
$H_2PO_4^-$	$S_{H_2PO_4^-}$	$\epsilon_p^{1.5} D_{H_2PO_4^-}$	$D_{H_2PO_4^-}$	0	0
HPO_4^{2-}	$S_{HPO_4^{2-}}$	$\epsilon_p^{1.5} D_{HPO_4^{2-}}$	$D_{HPO_4^{2-}}$	0	0
Ac^-	S_{Ac}	$\epsilon_p^{1.5} D_{Ac}$	D_{Ac}	$-\frac{i_a}{8FL_{B,a}}$	0

where D_i and ϵ_p indicate the diffusion coefficient of species *i* and the porosity of biofilm, respectively. The efficient diffusion coefficient is calculated according to the Bruggeman mode.

Section 6: calculation for the resistance of biofilms and solution

The resistance of biofilms is calculated by the following equation:

$$R = \frac{k_{bio}(L_{B,a} + L_{B,c})}{A}$$

where k_{bio} is the conductivity of the biofilms (the conductivity of the anode biofilm is thought to be equal to that of the cathode biofilm); $L_{B,a}$ and $L_{B,c}$ are the thickness of the anode and cathode biofilms, respectively; A is the area of the electrode.

The resistance of biofilms is calculated by the following equation:

$$R = \frac{k_l L_{Bulk}}{A}$$

where k_l is the conductivity of the solution; L_{Bulk} is the distance of the electrodes; A is the area of the electrode.

Section 7: variation of pH and acetate concentration during the operation of a CH_4-producing MES

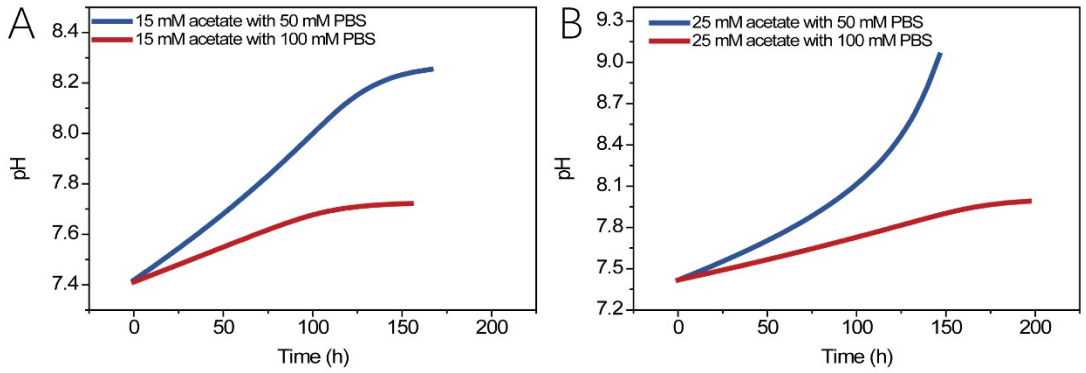

Fig. S3 pH value under typical operation conditions. (A): MESs are operated with 15 mmol L^{-1} initial concentration of acetate and 50 or 100 mmol L^{-1} PBS; (B): MESs are operated with 25 mmol L^{-1} initial concentration of acetate and 50 or 100 mmol L^{-1} PBS. mM indicates mmol L^{-1}

Ref.

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2. Li, J., et al., *Startup cathode potentials determine electron transfer behaviours of biocathodes catalysing CO_2 reduction to CH_4 in microbial electrosynthesis.* Journal of CO_2 Utilization, 2020. **35**: p. 169-175.
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5. Xiao, S., et al., *Parametric study of biocathodes in microbial electrosynthesis for CO_2 reduction to CH_4 with a direct electron transfer pathway.* Renewable Energy, 2020. **162**: p. 438-446.