

1 **Electronic Supplementary Information**

2 **Improved Performance of CEA Microbial Fuel Cells with** 3 **Increased Reactor Size**

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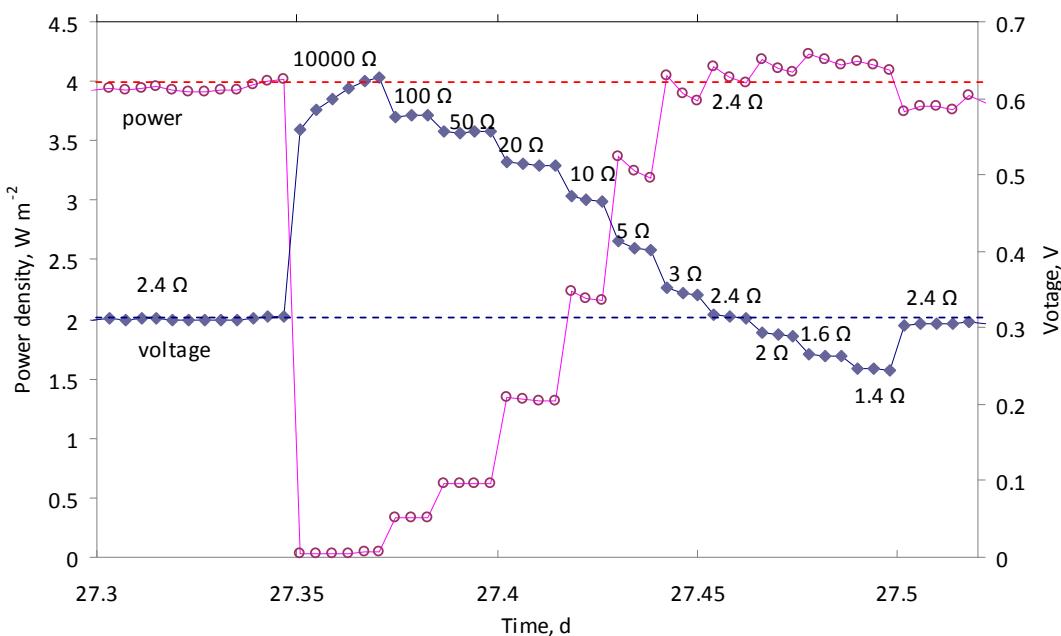
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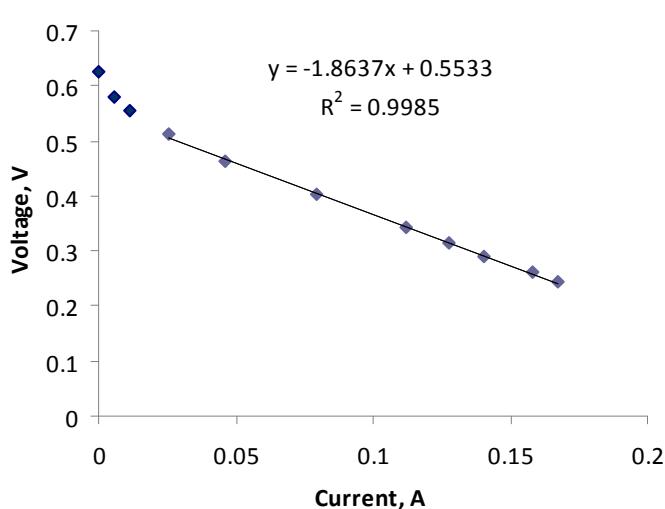
10 **1. Example of polarization curve preparation**

11 Fig. S1. demonstrates the voltage and power output of CEA1 during a polarization test.
12 CEA1 was connected to a precision decade resistance box with a resolution of 0.1Ω
13 (602-N, General Radio). Voltage was recorded every 6 minutes using a multichannel data
14 acquisition system (2700, Keithly, USA). The MFC produced an average power output of
15 3.95 W m^{-2} (3.12 V) when the external resistance was set at 2.4Ω before the polarization.
16 During polarization test, the external resistance was first set at $10 \text{ k}\Omega$ and stabilized for
17 about half hour. Then the external resistance was gradually reduced from 100 to 1.4Ω at
18 a rate of about 20 minutes per resistance. The last voltage reading at each resistance was
19 used to prepare the polarization curves.

20 The internal resistance of the MFC can be calculated based on the linear portion
21 ($0.026 - 0.167 \text{ A}$) of the voltage vs current curve (Fig. S2). The currents in the curve
22 were quotients of the last voltage readings at each resistance divided by the sum of the
23 external resistance and contact resistance (0.06Ω). The slope of the linear regression
24 (1.86Ω) is the internal resistance of the MFC at the current range. The maximum power
25 density (4.14 W m^{-2}) can be obtained from the power density vs current density curve
26 (Fig. S3).



35
36 **Fig. S1** Power density (red circle) and voltage (blue diamond) output during a
37 polarization test. The red and blue dashed horizontal lines indicate the power density and
38 voltage for an external resistance of 2.4 Ω in the polarization curves.
39



40
41 **Fig. S2** Voltage vs current curve for the calculation of internal resistance.

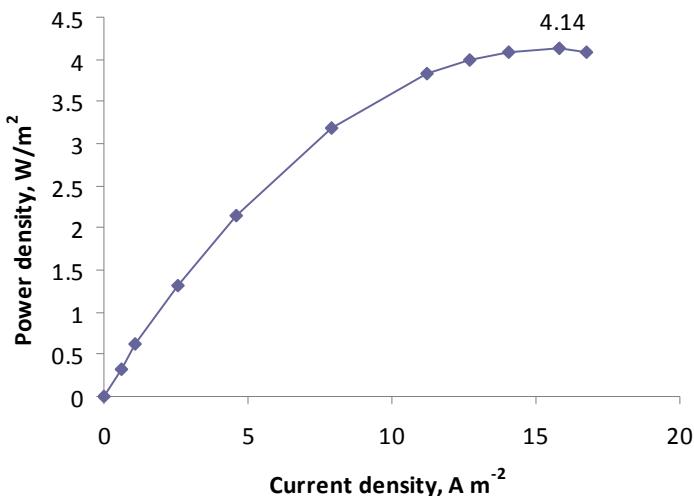


Fig. S3 Power density vs current density curve demonstrate the performance of the MFC.

Maximum power density is an important indicator of MFC performance. Linear sweep voltammetry (LSV) is commonly used in MFC studies to obtain polarization data and maximum power density, but high scan rates can significantly overestimate power production.^{1,2,3} However, no overestimation was noticed in the polarization by varying external resistances in this study, as about the same voltage and power density were obtained before and during polarization (Fig. S1). For example, the last voltage reading with an external resistance of 2.4Ω was 3.13 V, which was only slightly higher than the average voltage of 3.12 V before the polarization test. Therefore, the overestimation in power density was almost negligible with the method used in this study.

The major reason causing the difference in power overestimation is the different voltage reducing rates, as both techniques are the same in principle, i.e. recording current changes with the gradually reduced voltage (resistance). During the polarization tests in this study, the actual voltage reducing rate was 0.03 mV S^{-1} (Fig. S1), which is over 30 times slower than a common scanning rate of 1 mV S^{-1} in LSV. The slower voltage reducing rate reduces capacitive current, thus reducing the over estimation of current (power density).

2. Effects of water pressure and electrode location

Water pressure is critical for membrane-free air cathode MFCs as the PTFE gas diffusion layer can only hold about 10 cm (1 kPa) of water pressure based on a preliminary test. If the pressure is too high, water fills the pores in the layer, which significantly limits the diffusion of oxygen through it, resulting in low fuel cell performance, a phenomenon known as water flooding. If the pressure is too low, on the other hand, more air is sucked into the reactor, reducing the active three-phase interface of water-air-catalyst thus the performance of the cathode.

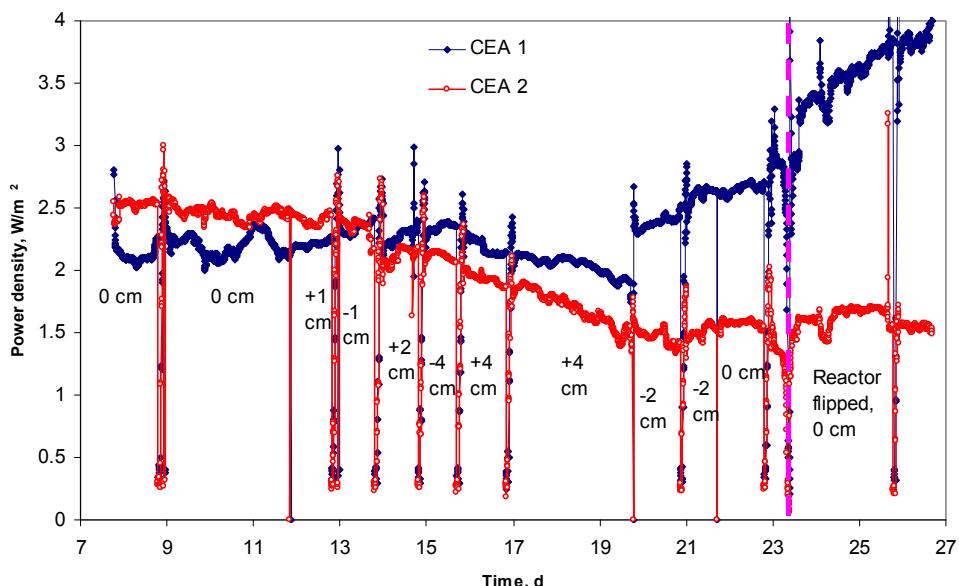
As demonstrated in Fig. S4, water pressure significantly affected the power output of the MFC. Although the trend was not very clear for the water pressure in the range of -

74 4 cm to +2 cm, the power densities of both CEA1 and CEA2 decreased significantly
75 when the water pressure was increased to +4 cm. The decreasing trend reversed (CEA1)
76 or stopped (CEA2) after the pressure was lowered to -2 cm. After the reactor was flipped
77 on the 24th day, the power density of CEA1 gradually increased from 2.8 W m⁻² to 4.1 W
78 m⁻² on the 27th day, while the power density of CEA2 remained about the same. The
79 power density of CEA1 was higher and less fluctuant at the bottom side of the reactor,
80 although the pressure difference between the two CEAs was very small as they were less
81 than 0.5 cm apart.

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83 Gradual decrease in the power density of CEA2 was probably due to the biogas
84 build-up between the anode and cathode, which was obvious during the open-cell
85 examination of the electrodes. The biogas build-up may greatly increase the spacing
86 between anode and cathode, thus significantly increasing the internal resistance and
87 reducing the power density. The openings in the CEA1 might be more effectively in
88 releasing the biogas produced, especially after the reactor was flipped with CEA1 at the
89 bottom (Fig. S4).

90



91

92 **Fig. S4** Effects of water pressure and electrode location on power generation. CEA1 had
93 been at the top side of the reactor and CEA2 the bottom side before the reactor was
94 flipped on the 24th day (pink dash line). The major power density spikes indicate where
95 polarization curves were conducted. The adjustment in water pressure followed right after
96 the finish of polarization experiments.

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Reference:

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