

1

- Supporting Information -

2 **Enhanced Electrochemical Reduction of Carbon Dioxide to**
3 **Formic Acid Using a Two-layer Gas Diffusion Electrode in**
4 **Microbial Electrolysis Cell**

5 Qinian Wang, Heng Dong*, Hongbing Yu*, Han Yu, Minghui Liu

6 College of Environmental Science and Engineering, Nankai University, No. 94

7 Weijin Road, Nankai District, Tianjin 300071, China

8 *Corresponding Authors; Phone: (86)22-23502756; Fax: (86)22-23502756; E-mail:

9 dongheng@nankai.edu.cn; hongbingyu1130@sina.com.

10

11

12

13

14

15

16

17

18

19

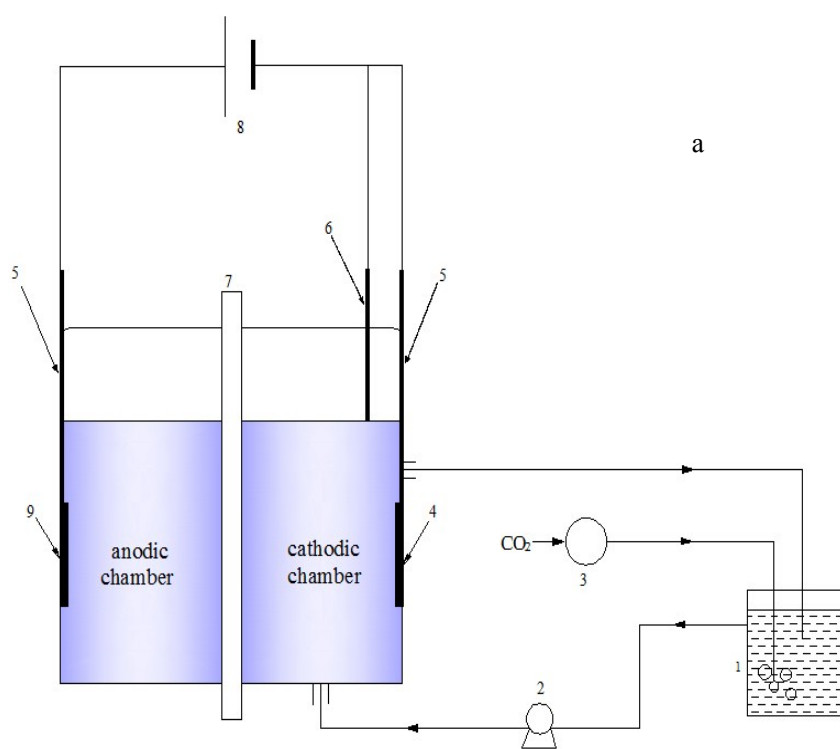
20

21

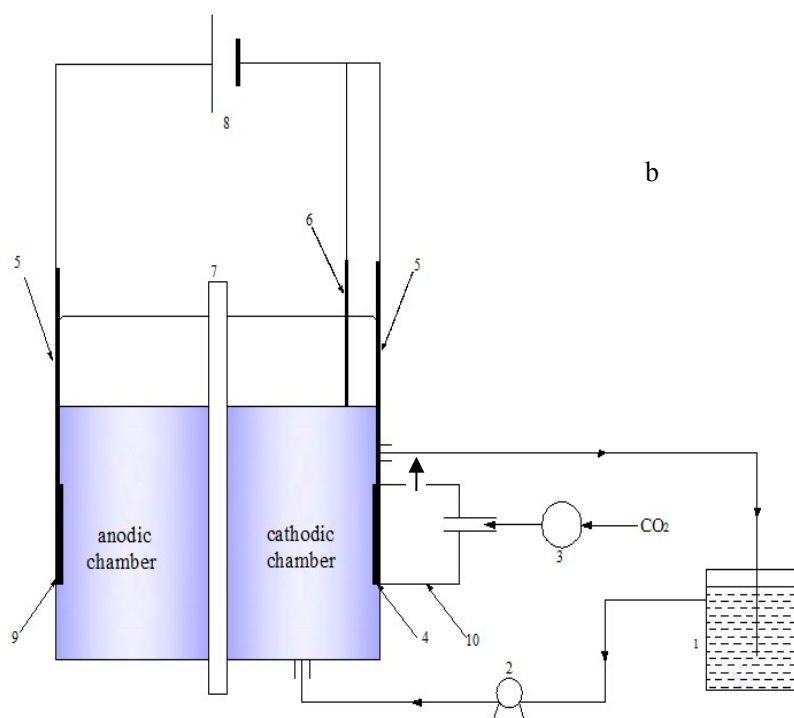
22

23 **Table S1** Simulated data of equivalent circuits for the Nyquist plots of impedance.

Electrode	E/V	R_S/Ω	$Q_1/$	n_1	R_1/Ω	$Q_2/$	n_2	R_2/Ω
			$\Omega^{-1} s^n cm^{-2}$			$\Omega^{-1} s^n cm^{-2}$		
SE	-1.2	1.431	4.154×10^{-5}	1	0.900	2.392×10^{-3}	0.782	20.730
	-1.3	1.421	4.160×10^{-5}	1	0.919	2.534×10^{-3}	0.778	9.101
SGDE	-1.2	1.290	1.143×10^{-6}	0.922	0.994	4.641×10^{-3}	0.732	16.030
	-1.3	1.307	8.046×10^{-5}	0.959	0.925	5.221×10^{-3}	0.712	8.143



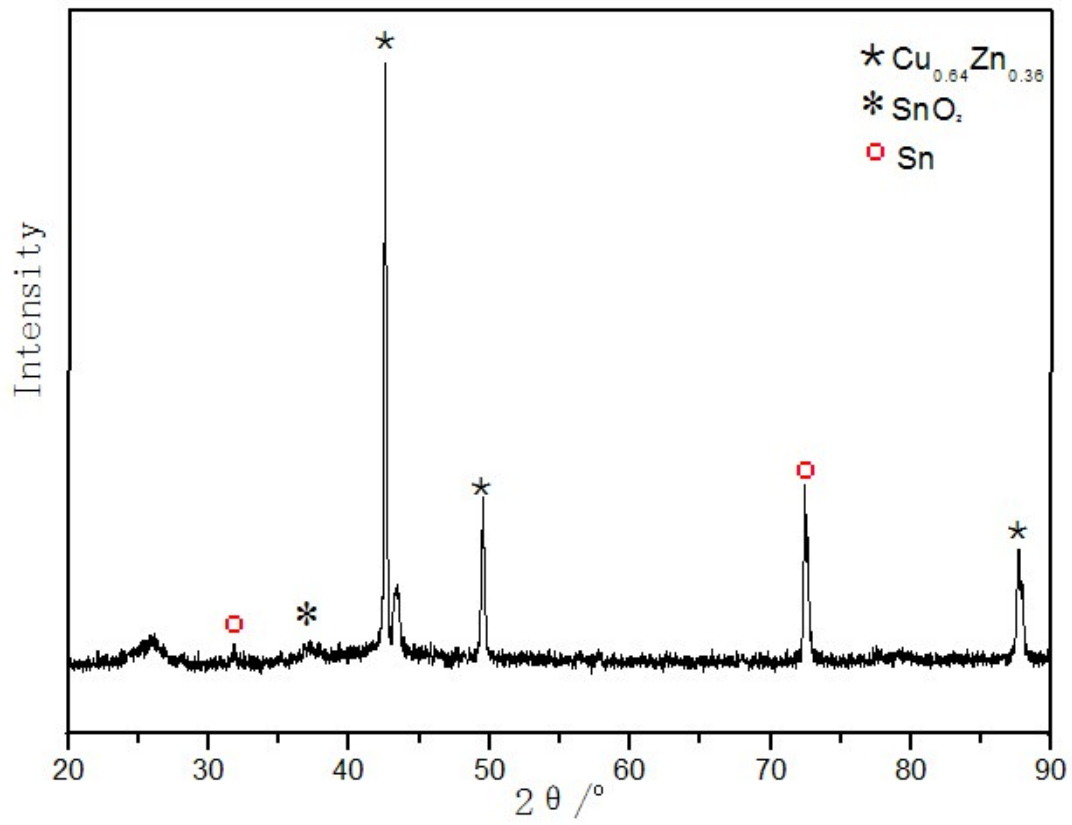
24



1 Electrolyte, 2 Pump, 3 Flowmeter, 4 Cathode (a: SE, b: SGDE), 5 Titanium wire, 6 Ag/AgCl electrode, 7 PEM, 8 Electrochemical workstation, 9 Anode, 10 Gas chamber.

25

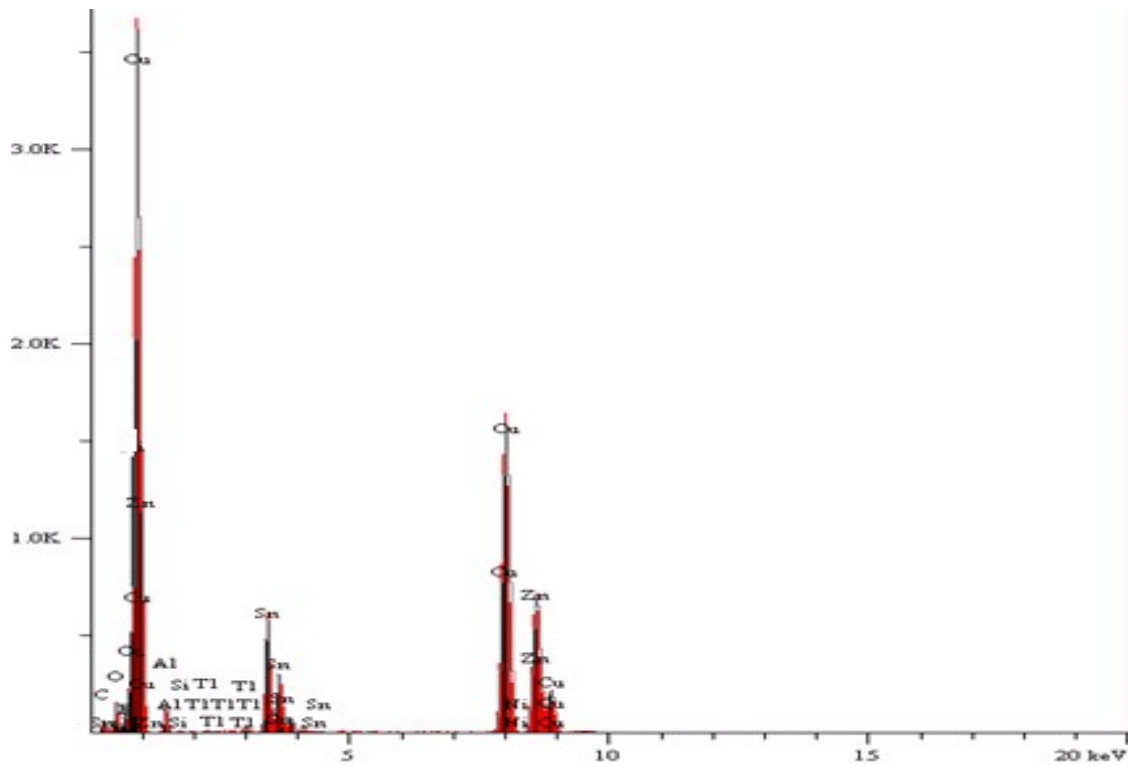
26 **Figure S1** Schematic overview of the MEC systems employed in this work. (a) MEC
 27 with the SE cathode: the catholyte was saturated with CO₂ before each electrolysis
 28 run, and CO₂ was continuously sparged into the catholyte during the electrolysis. (b)
 29 MEC with the SGDE cathode, CO₂ was continuously fed into the gas chamber during
 30 the electrolysis.



31

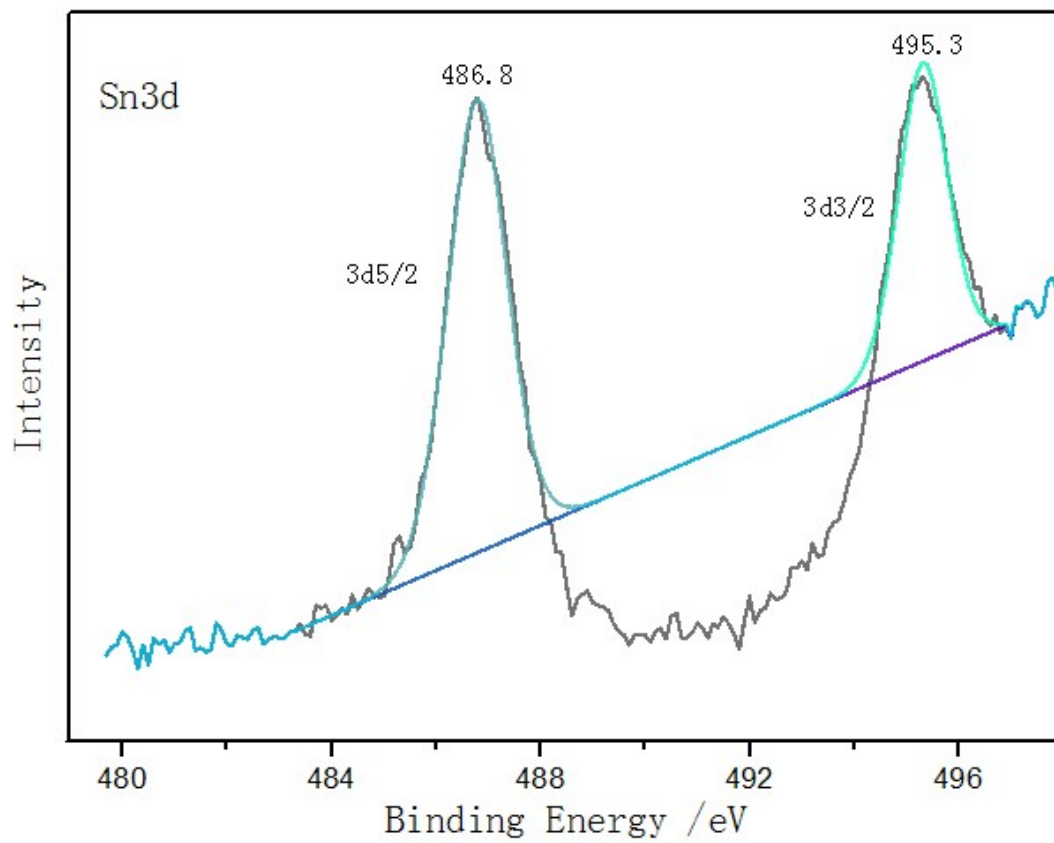
32 **Figure S2** XRD pattern of the SGDE. $\text{Cu}_{0.64}\text{Zn}_{0.36}$ is the major composition of the

33 brass mesh.



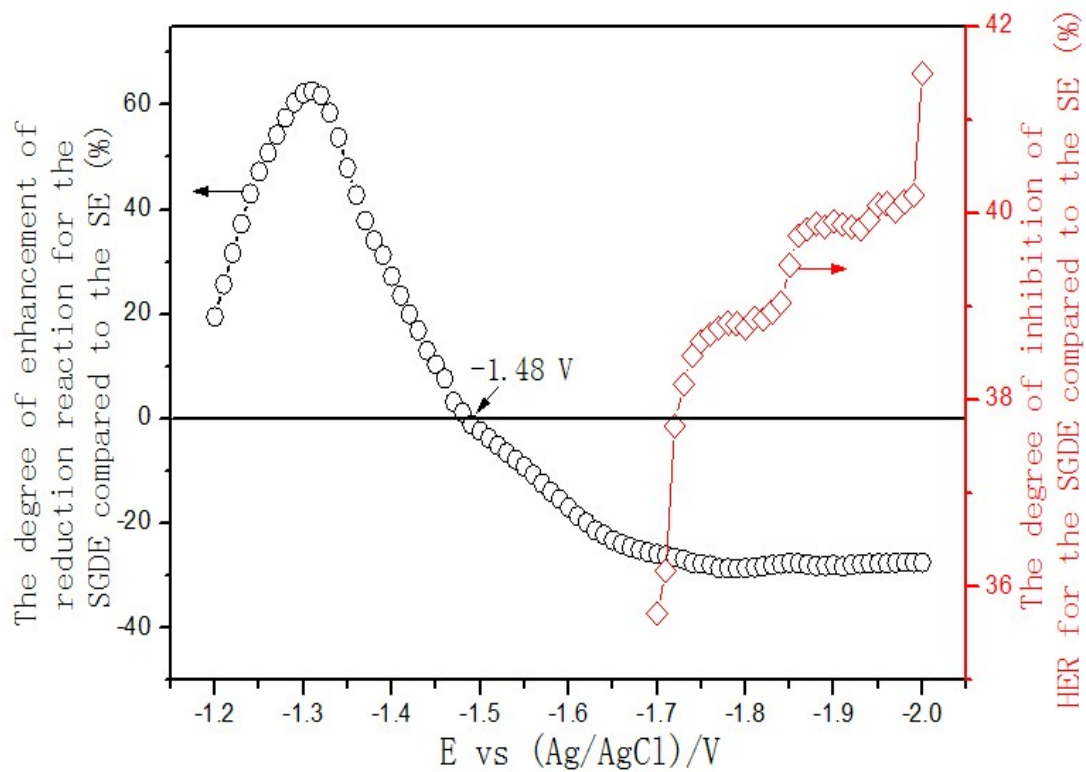
34

35 **Figure S3** EDX spectrum of the Sn-loaded brass mesh in the SGDE. Cu and Zn are
 36 the baseline elements of the brass mesh. Ni, Ti and Al are the impurities of the brass
 37 mesh.



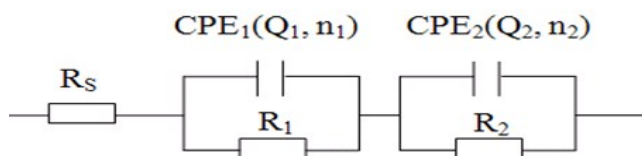
38

39 **Figure S4** XPS spectrum of Sn3d in the Sn-loaded brass mesh of the SGDE.



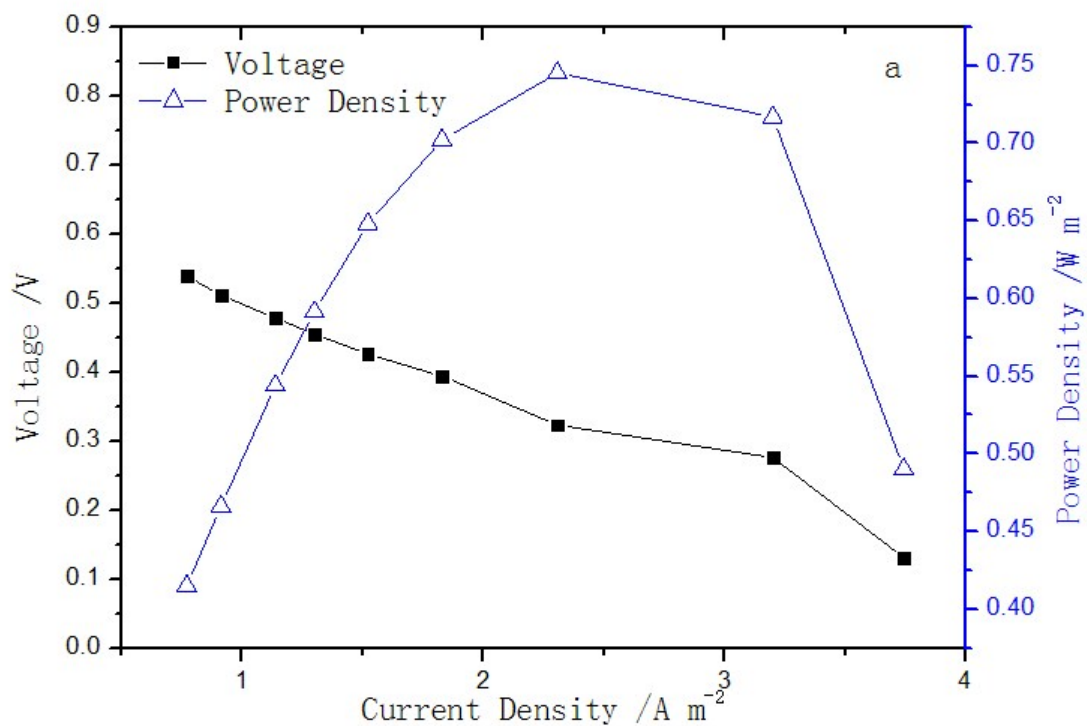
40

41 **Figure S5** The degree of inhibition of HER and of enhancement of reduction
 42 reactions for the SGDE compared to the SE.

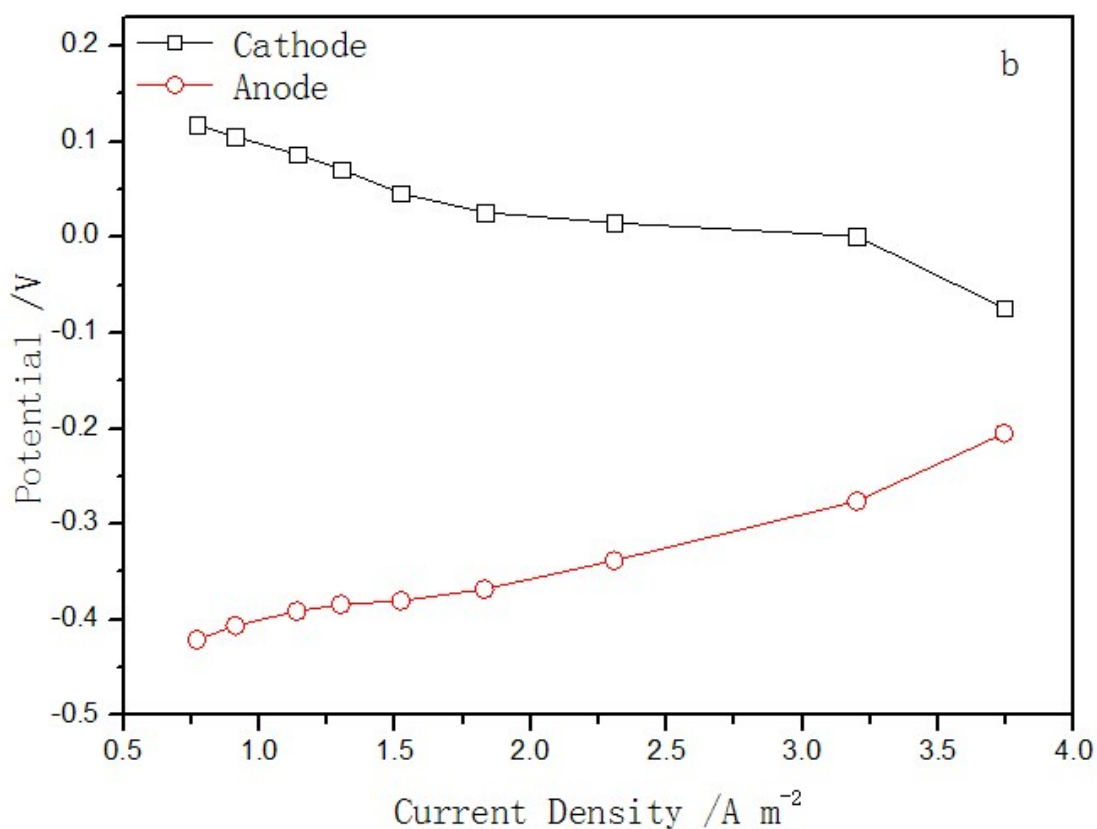


43

44 **Figure S6** Equivalent circuit used for fitting of the impedance. R_s : solution resistance,
 45 R_1 : interfacial ohmic resistance, R_2 : charge transfer resistance, CPE_1 and CPE_2 :
 46 constant phase element, Q_1 : CPE_1 value, Q_2 : CPE_2 value, n_1 : coefficient of CPE_1 , n_2 :
 47 coefficient of CPE_2 .



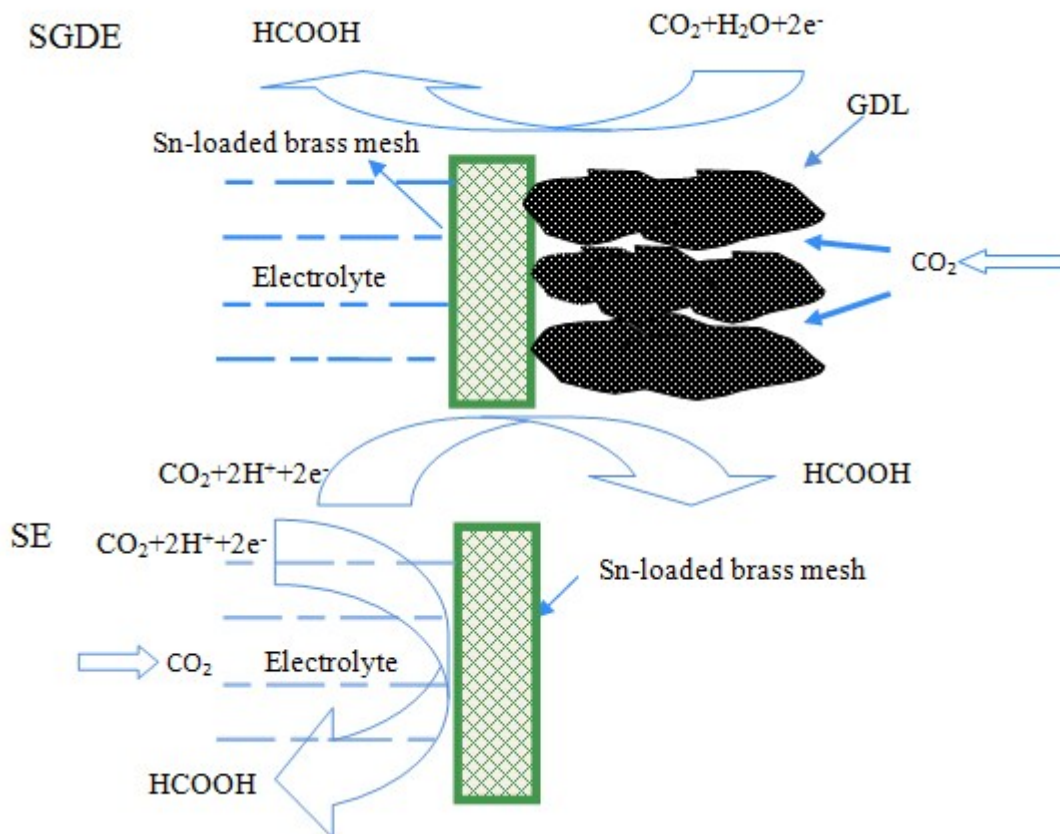
48



49

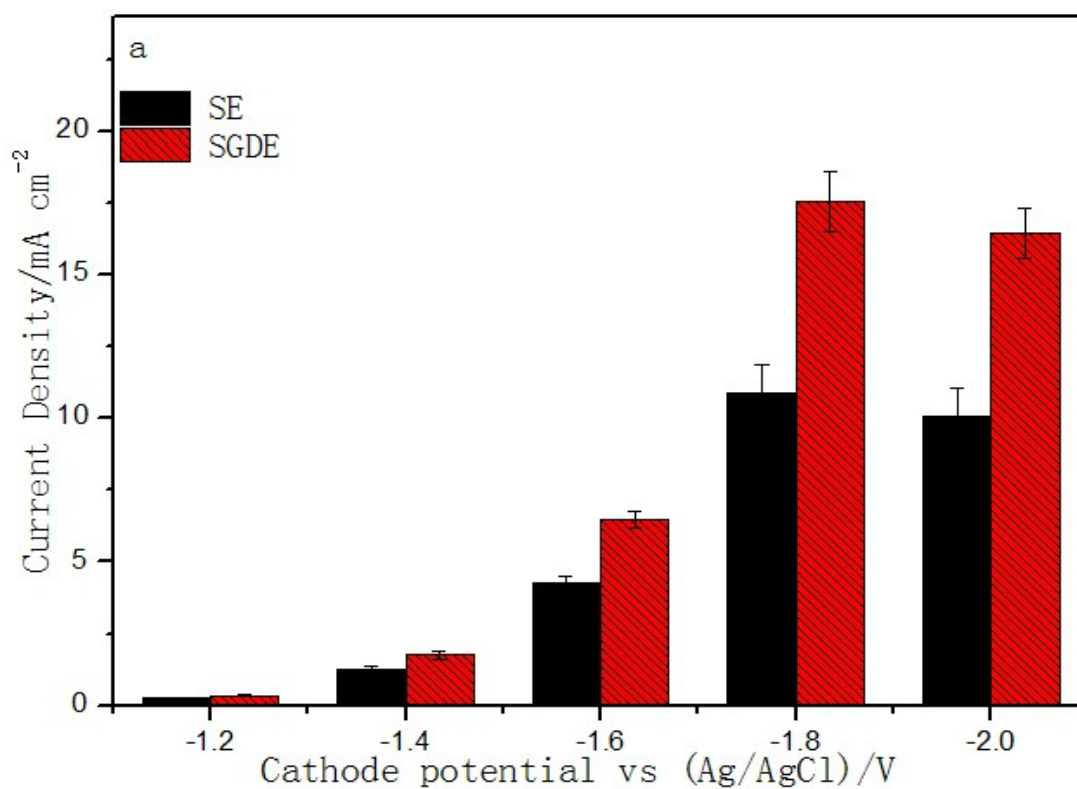
50 **Figure S7** Voltage and power density (a) and cathode and anode potential (b) of MFC

51 reactor vs. current density curves.

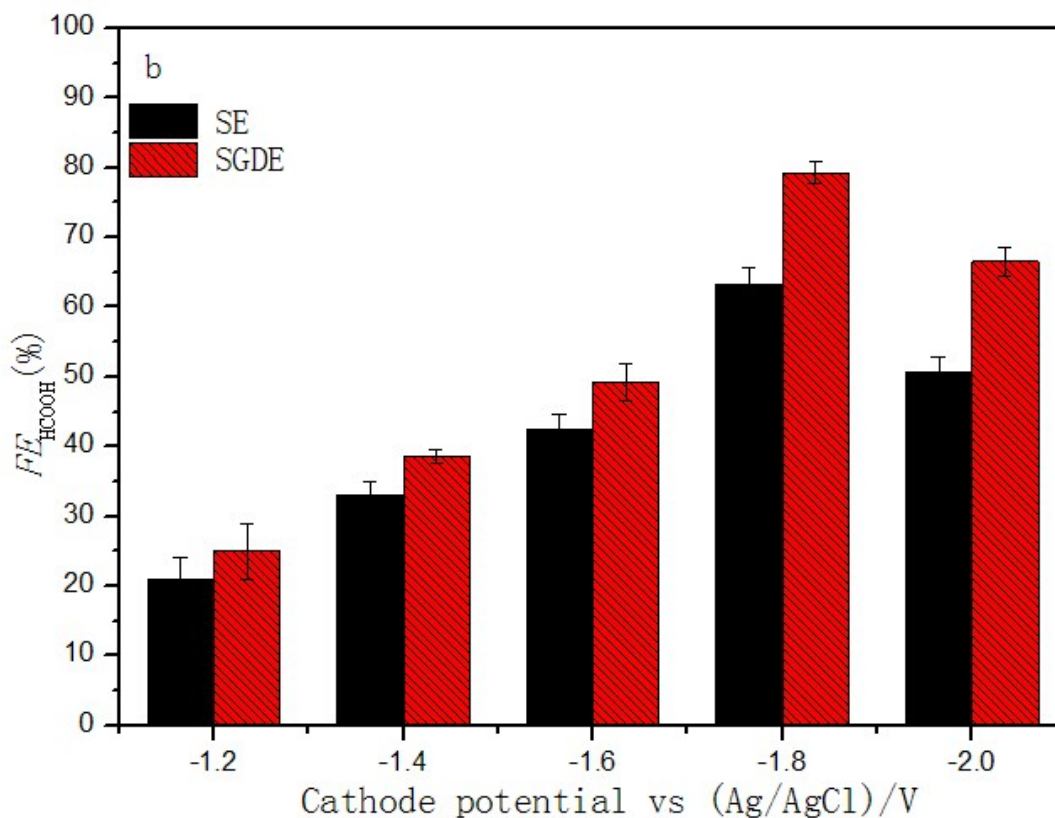


52

53 **Figure S8** Schematic of ERCF for the SGDE (upper) and the SE (lower).



54



55

56 **Figure S9** ERCF experimental results obtained with the SE and the SGDE in CEC.

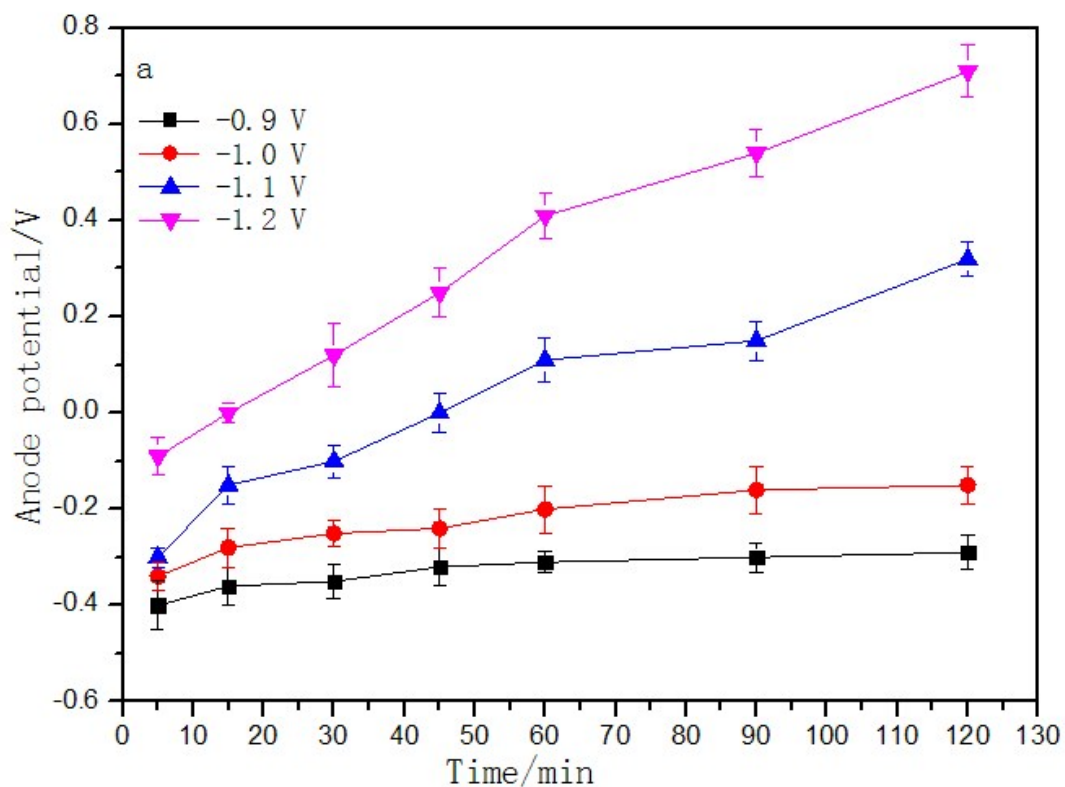
57 Current density is expressed as the current used for producing formic acid divided by
58 the geometric area of the SE and the SGDE.

59 It can be seen that formic acid can be detected from both electrodes at a cathode
60 potential of -1.2 V. Current density and FE_{HCOOH} increased when the cathode potential
61 shifted in negative direction to -1.8 V, but they decreased when the cathode potential
62 shifted from -1.8 V to -2.0 V. The FE_{HCOOH} value of 79.27 ± 1.52 % (at -1.8 V) is the
63 highest one reported in literature when using Sn electrodes under similar conditions ¹.

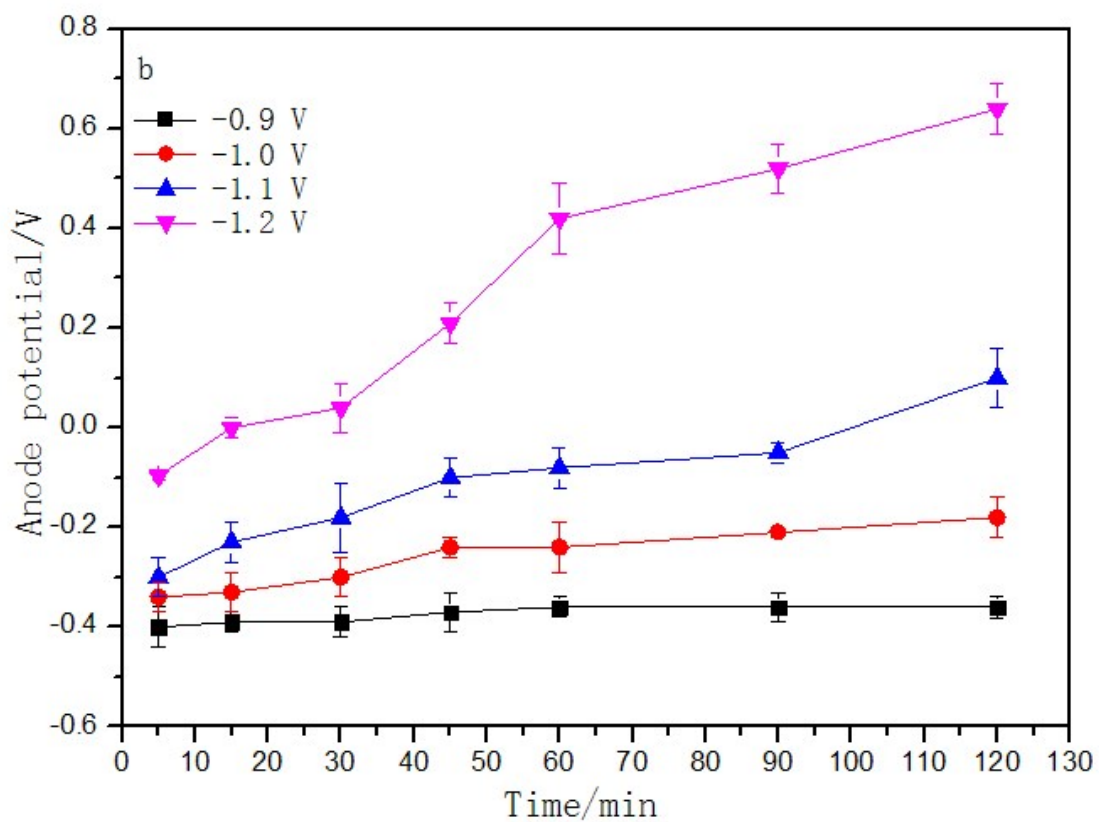
64 When the cathode potential was more positive than -1.8 V, ERCF became more slack
65 due to the low standard potential of CO_2/CO_2^- in aqueous media (-2.33 V vs SCE ²).

66 Whereas when it was more negative than -1.8 V, side reactions (such as HER)
67 emerged. This is in accordance with the CV results which showed that HER occurred

68 at cathode potential more negative than ca. -1.7 V.



69



70

71 **Figure S10** Dependence of the anode potential during ERCF run in MEC with the SE
72 cathode (a) and the SGDE cathode (b) on the applied cathode potential .

73 In a MEC system, with the assistance of the potential generated from microorganism
74 catalyzed anodic oxidation reaction, lesser power supply is needed to initiate ERCF
75 than that in a CEC. Meanwhile, the anode potential can influence the electron
76 liberating capacities of the microorganism ³. Therefore, the anode potential hold the
77 key to achieve higher product yield and FE_{HCOOH} at the cathode in our MEC systems.

78 In preliminary MEC experiments under constant cathode potential mode, we found
79 that the anode potential shifted to more positive values during the electrolysis and that
80 the shifting rate of the anode potential increased when the applied cathode potential
81 shifted to a more negative value. This may be attributed to the fact that the protons
82 and electrons released by the biodegradation of organic compounds in the anodic
83 chamber were unable to meet the needs of the cathode reaction ⁴. A high anode
84 potential will throttle the microorganism catalytic activity. We found that anodic
85 microorganisms were inactivated at an excessive positive potential (e.g. $> +1$ V) after
86 an electrolysis of 2 h in most of the cases. Hence, an electrolytic period of 2 h and an
87 applied cathode potential from -0.9 V to -1.2 V were adopted in this work for
88 protecting the microorganisms at the anode. After each ERCF test in MEC, the anode
89 microorganisms recovered in a short time. ERCF in MEC mode with the SGDE
90 cathode could be further enhanced by using advanced anode materials with larger
91 specific surface area, such as graphite brush.

92

93 **References**

- 94 1. J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem Soc Rev*, 2014, 43, 631-675.
- 95 2. V. Lates, A. Falch, A. Jordaan, R. Peach and R. J. Kriek, *Electrochimica Acta*, 2014, 128, 75-
96 84.
- 97 3. P. Aelterman, S. Freguia, J. Keller, W. Verstraete and K. Rabaey, *Applied Microbiology and*
98 *Biotechnology*, 2008, 78, 409-418.
- 99 4. Y. Zhan, Q. Wang, G. Yan and S. Guo, *CHEMICAL JOURNAL OF CHINESE*
100 *UNIVERSITIES-CHINESE EDITION*-, 2008, 29, 559.
- 101
- 102