Supporting Information

Encapsulation of living bioelectrode by hydrogel for

bioelectrochemical systems in alkaline media

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1. Experimental

Preparation of CB/SSM anode

Carbon black/stainless steel mesh (CB/SSM) composite electrodes were used as anodes in this study, which were prepared following previous report ¹. In a typical synthesis process, SSM (Hongye Stainless Steel Wire Cloth Co.,Ltd, Hengshui, Hebei, China, containing about 19% Cr and 9% Ni, mesh size of 50 and wire diameter of 0.20 mm) was firstly treated in 1 M H₂SO₄ for 24 h to obtain a rough surface, and to remove surface oxides and then was dipped into 5 g L⁻¹ Carbon black (CB) (VULCAN[®] XC72)/ethanol dispersion; after taking out from the dispersion the electrode was allowed to dry at room temperature. After dipping/drying process for three cycles, a CB/SSM composite electrode was obtained. The load of CB onto the SS was about 0.5 mg cm⁻² (normalized to the footprint area of SSM).

Fabrication of air-cathode

Gas diffusion layer: The hydrophobic gas diffusion layer (GDL) was prepared firstly by distributing 30 wt% carbon black (CB) (Vulcan XC-72R, Tengming Co. Ltd., Shanghai, China) into an appropriate amount of pore-former ethanol in a beaker and

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ultrasonic agitated for 30 min at 30 °C, followed by dripping 70 wt% polytetrafluoroethylene (PTFE) suspensions (60 wt%, Lusu Co. Ltd., Dongguan, China) into the blend slowly. After another 30 min, the blend was stirred and dried at 80 °C bath to give a dough-like paste. The paste was firstly rolled by a WQ-150D roll squeezer (Weiqing Co. Ltd., Dongguan, China) to form a gas diffusion film of 0.3 mm thickness and then it was rolled on one side of the stainless steel mesh. The sheet was then sintered for 25 min at 340 °C to melt the PTFE in order to form a fibrous three-dimensional structure for gas transport. This sheet was used as GDL in all the air-cathodes here.

Catalytic layer: Activated carbon (AC) was utilized as oxygen reduction catalyst to make catalytic layer (CL) of 0.2 mm thickness with PTFE (AC/PTFE ratio was 4/1). The fabrication procedure of CL is similar to GDL, and the sintering process of CL is avoided. The CL was rolled on the water facing side to obtain the final air-cathode with about 0.5 mm thickness.

Composition of trace metal and vitamin solutions ^{2, 3}:

Trace metal solution: 1.5 mg L⁻¹Nitrilotriacetic, 3 mg L⁻¹ MgSO₄·7H₂O, 0.5 mg L⁻¹ MnSO₄·H₂O, 1 mg L⁻¹ NaCl, 0.1 mg L⁻¹ FeSO₄·7H₂O, 0.18 mg L⁻¹CoSO₄·2H₂O, 0.1 mg L⁻¹CaCl₂·2H₂O, 0.18 mg L⁻¹ZnSO₄·7H₂O, 0.01 mg L⁻¹CuSO₄·5H₂O, 0.02 mg L⁻¹ KAl(SO₄)₂·12H₂O, 0.01 mg L⁻¹H₃BO₃, 0.01 mg L⁻¹ NaMoO₄·H₂O, 0.025 mg L⁻¹NiCl₂·6H₂O, 0.003 mg L⁻¹NaSeO₃·5H₂O.

Vitamin solution: 2 mg L⁻¹ Biotin, 2 mg L⁻¹ Folic acid, 10 mg L⁻¹ Pyridoxine-HCl, 5 mg L⁻¹ Thiamine-HCl·2H₂O, 5 mg L⁻¹ Riboflavin, 5 mg L⁻¹ Nicotinic, 5 mg L⁻¹ D-Capantothenate, 0.1 mg L⁻¹ Vitamin B₁₂, 5 mg L⁻¹ P-Aminobenzoic acid, 5 mg L⁻¹ Lipoic acid.

2. Mathematical derivation



A mass balance of the acetate (or hydroxyl ion) at the biofilms surface is expressed as the sum of the acetate that diffused from solution through the hydrogel and the consumed by the biofilms:

$$V \frac{dC_b}{dt} = J_d A J_c A$$
$$= \frac{AD_d}{\delta_{hydrogel}} (C_s - C_b) - \frac{AD_c}{\delta_{biofilm}} C_b$$

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When $\frac{dC_b}{dt} = 0$, means that the diffusion rate of acetate (or proton) across the hydrogel was equal to its consuming rate in the biofilms, the concentration of acetate (or hydroxyl ion) at the biofilm surface is invariable,

that case,
$$\frac{AD_d}{\delta_{hydrogel}} (C_s - C_b) - \frac{AD_c}{\delta_{biofilm}} C_b = 0$$

Then, the relationship between the C_b and C_s is:

$$C_{b} = \frac{D_{d}C_{s}}{D_{d} + \delta_{hydrogel}B}$$

$$B = \frac{D_{c}}{D_{d}}$$
(1)

(in which $\delta_{biofilm}$ is the consuming rate of acetate in the biofilms)

When the $\delta_{hydrogel}=0$, means the solution-biloelectrode (*SBE*), then the $C_b = C_s$. In the hydrogel-bioelectrode (*HBE*), the $\delta_{hydrogel}>0$, the C_b is lower than the C_s .

3. Supplementary data

Table S1 Performance of HBE and SBE under different conditions

HBE				SBE			
^a Feeding solution		j	P _{max}	Feeding solution		j	P _{max}
Cacetate	pН	/mA cm ⁻	/ mW m ⁻	Cacetate	рН	/mA cm ⁻	/ mW m-
/mM	-	2	2	/mM		2	2
20	7.0	0.28	759	20	7.0	1.33	1269
20	8.0	0.53	875	20	8.0	0.91	860
20	9.0	0.61	1002	20	9.0	0	0
20	10.0	0.64	1116	20	10.0	0	0
20	11.0	0.67	1120	20	11.0	0	0
20	12.0	0	0	20	12.0	0	0
40	10.0	0.65	1156	40	7.0	1.29	1271
60	10.0	0.80	1328	60	7.0	1.29	
80	10.0	0.87	1350	80	7.0	0.92	
100	10.0	0.90	955	100	7.0	0.77	
120	10.0	0.81		120	7.0	0.27	
^a The feeding solution is 100 mM PBS							

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PVA	*Swelling ratio	Diffusive coefficient / cm ² s ⁻¹				
conc.	/ %	proton	hydroxyl ion	acetate		
6%	538	5.14*10-6	2.55*10-6	1.49*10-6		
8%	524	5.63*10-6	3.11*10-6	1.91*10 ⁻⁶		
10%	499	6.75*10-6	3.51*10-6	2.53*10-6		
12%	442	6.78*10-6	3.87*10-6	2.81*10-6		
15%	409	6.17*10 ⁻⁶	3.90*10 ⁻⁶	2.41*10 ⁻⁶		
18%	351	7.50*10 ⁻⁶	4.62*10 ⁻⁶	2.43*10 ⁻⁶		

Table S2 The properties of PVA hydrogel prepared from different concentration of PVA solutions

*Swelling ratio at distilled water with pH value of 7.0.

Table S3 Swelling capacity of PVA hydrogel in 100 mM PBS solutions at different

pH at 25 °C.

рН	Swelling ratio / %
7	483
8	380
9	325
10	292
11	222
12	220



Fig. S1 Schematic diagram of the fabrication of HBE



Figure S2. Scanning electron microscopy images of biofilms in CB/SSM electrode



Figure S3 Cell polarization and power density curves of MFCs using SBE at PBS with pH=7.0 and different acetate concentration

References

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