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Opening size optimization of metal matrix in rolling-pressed activated carbon air–cathode for microbial fuel cells

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HIGHLIGHTS

- A power density of 2151 mW m^{-2} was achieved using an optimized matrix of 40 mesh.
- Power exhibited the same trend as that of linear sweep voltammetry at −0.2 to 0 V.
- An optimized matrix can significantly decrease the charge transfer resistance.
- Mesh density had a better correlationship with power density than opening size.

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ABSTRACT

Stainless steel mesh (SSM) with four opening sizes (20–80 M) were investigated as matrixes of activated carbon air–cathodes in microbial fuel cells (MFCs). The highest power density of 2151 ± 109 mW m^{-2} (at 5.54 ± 0.14 A m^{-2}) was obtained using 40 M, with a value 45% higher than 1485 ± 18 mW m^{-2} of 80 M. The trend of linear sweep voltammetries were in accordant with power output over a cathodic potential range from −0.2 to 0 V. The differences in performance were attributed to the internal resistances. Charge transfer resistance (R_{ct}) was the dominant internal resistance in most of air–cathodes, with the lowest value of 2 Ω in 40 M. Density of metal mesh exhibited a more significant correlationship with maximum power densities (R^2 = 0.9222) compared to opening size (R^2 = 0.7068), demonstrated that the density of metal current collector was vital to the performance of cathodes.

1. Introduction

Microbial fuel cells (MFCs) are recognized as a green power generation technology because any sources of biodegradable organic matters, including simple molecules (such as carbohydrates and proteins) as well as complex mixtures (such as brewery wastewater and corn stover) [1–6], can be theoretically used in MFCs for power generation based on the catalysis of living microorganisms [7,8]. In addition to improving the catalytic activity of the anaerobic bio-anode and reducing the ohmic resistance of the electrolyte to a minimum [9], to improve the performance of the cathode is a relevant way to significantly increase the power of MFCs. The combination of a refined microbial anode and a robust cathode together with an optimized fuel cell configuration can be a realizable design for high power MFCs.

Activated carbon air–cathode (ACAC) is such a robust and highly efficient cathode with advantages of low cost (30 $ m^{-2} compared to 1600 $ m^{-2} of Pt–Nafion cathode) and high reproducibility [10,11]. This cathode is promising to be applied in a large scale, compared to those made of expensive catalysts (typically Pt) and binders (usually Nafion) [12–16]. Gas diffusion layer (GDL), catalyst layer (CL) and current collector (CC) are main elements of an ACAC. Both GDL and CL had been systematically investigated previously to maximize the performance under minimum losses [17–19]. However, the CC in ACAC had not been thoroughly studied so far.

To reduce electrode ohmic losses, electrodes (such as graphite and carbon) need to be supported by a highly conductive metal CC. Several kinds metal mesh had been applied, such as Ni mesh [20], Ni foam [21], Al-alloy mesh [22], Ti mesh [23], copper mesh [24] and stainless steel mesh (SSM) [25–28]. The stainless steel mesh was usually used as the CC in air–cathodes because it is inexpensive and relatively anticorrosion. The properties of SSM, such as mesh (opening size) and density, was closely related to the

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performance by affecting the oxygen transfer, ion transfer and electrical conductivity between the CL and metal surface. Besides, an overview of the estimated capital costs of bioelectrochemical systems based on materials currently used in laboratory systems showed that the cost proportion of CC was 4.7%, while this percentage was predicted to be 40% based on inexpensive materials in the future [7]. While in our ACAC, the cost of CC approximately takes 65% of total cost. Thus the CC need to be paid more attention. The effect of different mesh on power generation has been examined in a cathode using Pt catalyst, poly(dimethylsiloxane) (PDMS) binder and brushing method [29]. They found that the power density increased with an increase of mesh opening size, as the result of best performance of 30 M and 50 M. However, these results are obtained in a different cathode and therefore they cannot be directly translatable to the performance of our newly developed rolling-pressed ACAC. Here the performance of ACACs made of different mesh SSM with activated carbon catalyst, polytetrafluoroethylen (PTFE) binder and rolling method was investigated. The electrochemical characteristics of different cathodes were compared and analyzed, in terms of linear sweep voltammetry (LSV), Tafel plot and electrochemical impedance spectrum (EIS). The performance including maximum power densities (MPDs), polarization curve, anodes/cathodes potentials and Coulombic Efficiency (CE) was also evaluated.

2. Materials and methods

2.1. Cathodes

Cathodes were made by rolling-press method according to procedures previously described [28]. All the cathodes were consisted of a SSM with a CL rolled on the water facing side and a GDL rolled on the air facing side. The mesh opening sizes of SSM were: 20, 40, 60 and 80 (type 304, Detiannuo Commercial Trade Co. Ltd., Tianjin, China). The corresponding air–cathodes were marked as 20 M, 40 M, 60 M and 80 M. The GDL was made of carbon black (Jinqiushi Chemical Co. Ltd., Tianjin, China) and PTFE emulsion (60 wt%, Hesen, Shanghai, China) with a mass ratio of 3:7, followed by heating at 340 °C for 20 min. The CL was made of activated carbon (Xinsen Carbon Co. Ltd., Fujian, China) and PTFE emulsion with a mass ratio of 6:1. The air–cathodes sheets were dried at room temperature for least 24 h before installed in MFCs.

2.2. MFC construction and operation

MFCs were single-chamber cubic-shaped reactors constructed as previously described (4 cm long and 3 cm in diameter) [28]. Acetone cleaned carbon fiber brush (25 mm in diameter) was employed as the anode [30]. All reactors were inoculated by the effluent from an MFC operated for over one year. The medium was a phosphate buffer nutrient solution (PBS) containing: $Na_2HPO_4{\cdot}12H_2O$, 10.317 g L^{-1}; $NaH_2PHO_4{\cdot}2H_2O$ 3.321 g L^{-1}; NH_4Cl 0.31 g L^{-1}; KCl 0.13 g L^{-1}; trace minerals (12.5 mL L^{-1}) and vitamins (5 mL L^{-1}) contained 1.0 g L^{-1} of sodium acetate as the fuel [28]. Reactors were refilled each time when the voltage decreased to less than 50 mV at 30 °C, forming a complete cycle.

2.3. Electrochemical analysis

Cell voltages across 1 kΩ were recorded every minute using a data acquisition system (PISO-813, ICP DAS Co., Ltd.). Polarization curves were performed at the 3rd cycle when anodes were well acclimated. Polarization and power density curves were obtained by varying the external resistance from 1000 to 30 Ω with a time interval of 25 min to ensure a stable voltage.

Cathodes were soaked in 50 mM PBS in abiotic reactors for at least 24 h before electrochemical tests. The target cathode (project area = 7 cm^2) and a platinum sheet of 1 cm^2 were used as the working electrode and the counter electrode. The reference electrode was saturated calomel electrodes (3 M KCl, 0.241 V versus standard hydrogen electrode). In order to avoid the undesirable losses on measurements, all the electrochemical tests were performed in the same reactor using a firmly fixed reference electrode. Reactors were refilled each time with the same electrolyte.

LSV was conducted from 0.3 to −0.2 V with a scan rate of 0.1 mV s^{-1}. Tafel plots (log |current density|, A m^{-2}, versus |overpotential|, V) were recorded by sweeping the overpotential ($|\eta|$, mV) from 0 to 100 mV at 0.1 mV s^{-1}, where $\eta = 0$ is the open circuit potential (OCP).

EIS was performed over a frequency range of 100 kHz to 10 mHz with a sinusoidal perturbation signal amplitude of 10 mV using a potentiostat (Autolab PGSTAT 302N, Metrohm, Switzerland). In order to evaluate the performance of each electrode with different overpotentials, the initial potential was set at the overpotential of 0 V, 0.1 V, 0.2 V and 0.3 V in turn as previously used by us [28]. The Nyquist plots were used to interpret the spectra. A least-squares fitting program (ZsimpWin 3.10) was employed to simulate plots according to an equivalent circuit (Fig. S2).

3. Results

3.1. Performance of the four different air–cathodes

Six cycles after inoculation, maximum voltages were obtained in all MFCs. MPDs decreased as follow: 40 M (2151 ± 109 mW m^{-2} at 5.54 ± 0.14 A m^{-2}) >60 M (1993 ± 53 mW m^{-2} at 5.34 ± 0.07 A m^{-2}) >20 M (1970 ± 137 mW m^{-2} at 7.50 ± 0.26 A m^{-2})

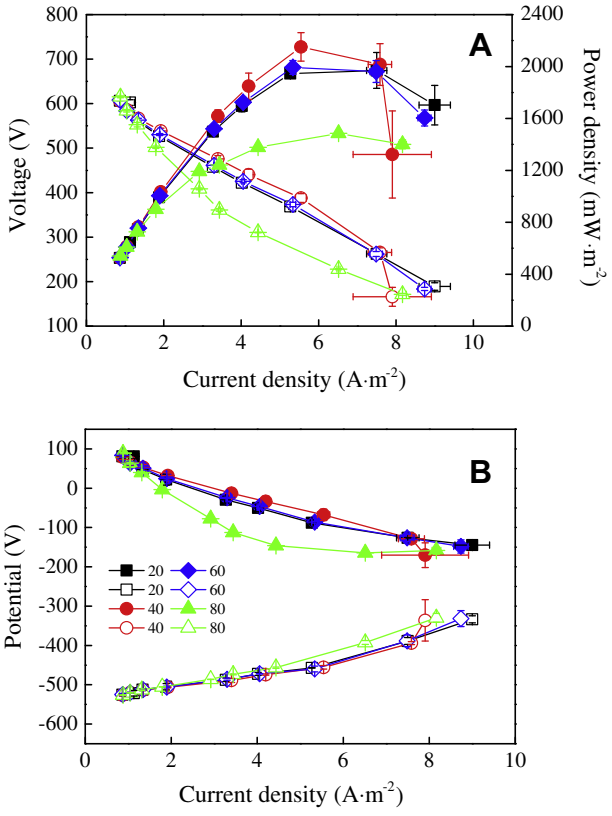

Fig. 1. Polarization and power density curves (A) and electrode potentials (B) of four air–cathodes using different matrix.