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Short communication

The use of double-sided cloth without diffusion layers as air-cathode in microbial fuel cells

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ABSTRACT

The cost of electrode materials is one of the most important factors limiting the scale of microbial fuel cells (MFCs). In this study, a novel double-sided cloth (DC) without diffusion layer is using as air-cathode, which decreases the cost and simplifies electrode production process. Using Pt as catalyst, the maximum power density of MFC using DC cathode is $0.70 \pm 0.02\,W\,m^{-2}$, which is similar to that obtained using carbon cloth (CC) cathodes ($0.66 \pm 0.01\,W\,m^{-2}$). After running in stable status, the Coulombic efficiencies (CEs) ($18 \pm 1\%$) and COD removal rates ($75 \pm 3\%$) are almost the same as those of CC cathode with diffusion layers. Using carbon powder as catalyst on the DC cathode, the maximum powder density is $0.41 \pm 0.01\,W\,m^{-2}$, with a COD removal rate of $66 \pm 2\%$ and a CE of $13.9 \pm 0.5\%$. The total cost of cathode based on power output decreases as follows: CC with Pt (CC-Pt, 2652$ W^{-1}), DC with Pt (DC-Pt, 1007$ W^{-1}) and DC with carbon powder (DC-C, 22$ W^{-1}), showing that DC is an inexpensive and promising cathode material for future applications.

1. Introduction

Microbial fuel cell (MFC) is an innovative and challenging research field which has extensive development and applicable perspective in various fields, such as alternative energy, biological sensor, and energy sustainable water infrastructure [1,2]. However, the high capital cost and low power output restrict the further development and application of MFCs. Thus, improving power output and reducing costs are two main challenges that researchers should be faced with [3].

The cost of MFC mainly depends on the design of reactors. A typical MFC includes the anode, the cathode and the separator. In 2004, Liu and Logan found that separator can be removed from the system to decrease the cost and improve the power output [4]. In this membrane-less system, the cost and performance of electrodes become much more essential when considering for application. Recent research indicated that the traditional high cost anode material (such as carbon cloth) can be replaced by an inexpensive carbon mesh (10–40$ m^{-2}) with power densities increased by 7% [5]. However, the research indicated that carbon mesh did not appear possible as cathode material because the loose weave made it hard to apply uniform diffusion layers to prevent the water leakage. Therefore, the inexpensive and hydrophobic air-cathode material is needed to be developed.

The air-cathode of membrane-less MFC needs the cathode matrix, catalyst, catalyst binder and diffusion layers to form a favorable three-phase interface [6], and therefore the cost of the MFC is mainly focused on the cathode [7]. It was reported that the costs of anodic and cathodic matrices accounted for 9.4% and 47% of total cost of MFCs, showing that the development of matrix material was extremely significant for future applications [7]. The nature of the cathodic matrix had a significant influence on electron transfer of air-cathode MFC, therefore the cathodic matrix should have excellent performance on conductivity for electron transfer and sufficient intensity to sustain water pressure. In previous studies, various carbon-based materials, including carbon paper [8], carbon cloth [6], graphite cloth [9], etc., were widely used as cathode matrix. Since carbon paper and carbon cloth are very expensive (1000$ m^{-2}), the high cost limits the extensive application of MFCs. Inexpensive stainless steel mesh [10–12], nickel mesh [11] and canvas cloth [13] were recently demonstrated as cathode matrix, which significantly reduced the cost of electrode. Cheng et al. found that the application of PTFE and carbon powder as diffusion layers increased power output and CE [6], however, simultaneously increased the cost of cathode manufacture.

The double-sided cloth was constructed by hydrophobic polyester fiber cloth on both sides with hydrophobic polyurethane

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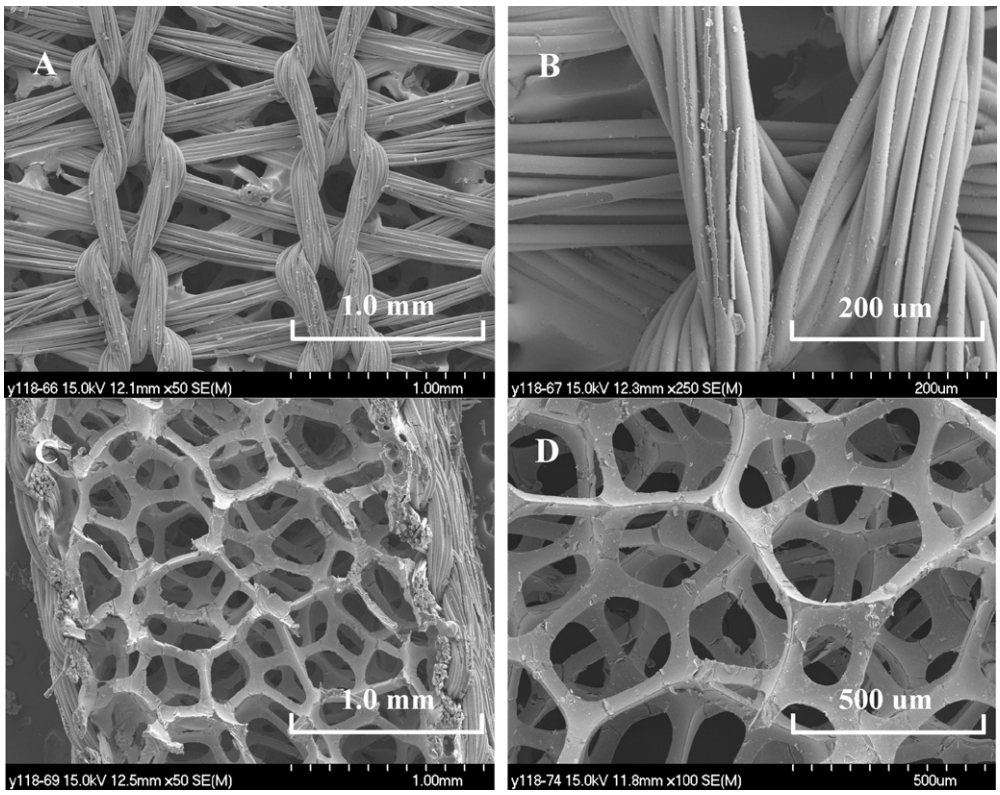

Fig. 1. Scanning electron microscope (SEM) images of surface matrix (A and B) and inner matrix (C and D) of double-sided cloth.

sponge backing and coated with corrosion-resistance conductive nickel–copper alloy. It was used in electromagnetic shielding and has the additional advantages of being a certain thickness, hydrophobicity and excellent conductivity. In this study, the double-sided cloth was used as the cathode matrix in single chambered air-cathode MFCs without application of diffusion layer. The performance of the MFC was evaluated in terms of maximum power densities, COD removal rates, Coulombic efficiencies (CEs), oxygen permeability and costs for reactors using Pt and carbon powders as two different oxygen reduction catalysts.

2. Materials and methods

2.1. Electrodes

All the anodes were made of non-wet proofed carbon cloth (E-TEK, USA). Hydrophobic double-sided cloth (DC, Canafull Industry Co., Ltd.) without diffusion layers was used as matrix of cathodes, containing 0.35 mg cm^{-2} of Pt (C1-10 10% HP Pt on Vulcan XC-72, BASF, USA) or carbon powder (Nantong, China) as catalyst on the water facing side. Carbon cloth (CC) cathodes with a carbon base layer and four PTFE (Dupont, USA) diffusion layers were made as positive control (0.35 mg Pt cm^{-2}, Nafion binder) [4,6].

2.2. MFC setup and operation

According to previous studies, single chambered cubic MFCs were constructed and operated at 1000 Ω external resistor except as noted [4]. MFCs were inoculated with domestic wastewater, with acetate (1.0 g L^{-1}) as energy source in 50 mM phosphate buffer solution (PBS, pH 7.0) and mineral (12.5 mL L^{-1}) and vitamin (5 mL L^{-1}) solutions [14]. Each reactor had a duplicate, all the reactors were operated at 30 °C in a constant temperature room.

2.3. Chemical and electrochemical analyses

X-ray diffraction (XRD) analysis was carried out with the D/maxrB diffractometer (Japan) using a Cu Kα X-ray source (45 kV, 40 mA). Energy dispersive X-ray spectroscopy (EDS) was performed to analyze the elemental composition (15 kV), with the Hitachi-S-4700 analyzer coupled to a scanning electron microscope (SEM, Hitachi Ltd. S-4700). Diffusion coefficient was measured by fixing a nonconsumptive fiberoptic dissolved oxygen (DO) probe (FOXY, Ocean Optics Inc., Dunedin, FL) in the center of the single-chamber MFC filled with deionizer water. The water used for DO tests was degassed by stirring in an anaerobic box (mini MACS, DWS) for at least 48 h to remove oxygen. Before each measurement, the probe was calibrated by two point method [15].

2.4. Calculations

Cell voltage was recorded every 30 min using a data acquisition system (PISO-813, ICP DAS Co., Ltd.). Current density (i, A m^{-2}), power density (P, W m^{-2}), Coulombic efficiency (CE) and COD removal rate were calculated as previously described [6]. Polarization curves were obtained by varying external resistances from 50,000 to 50 Ω, with each resistor tested for 30 min. Oxygen permeability was measured in terms of oxygen transfer coefficient as previously described [6]. The total cost of cathode based on power output was calculated as cost/P_{max} ($ W^{-1}).

3. Results and discussion

3.1. Characteristics of double-sided cloth

The surface morphology of the double-sided cloth (DC) was investigated by SEM. The DC consisted of the surface and the inner matrix (Fig. 1), with a thickness of 2 mm. The sur-

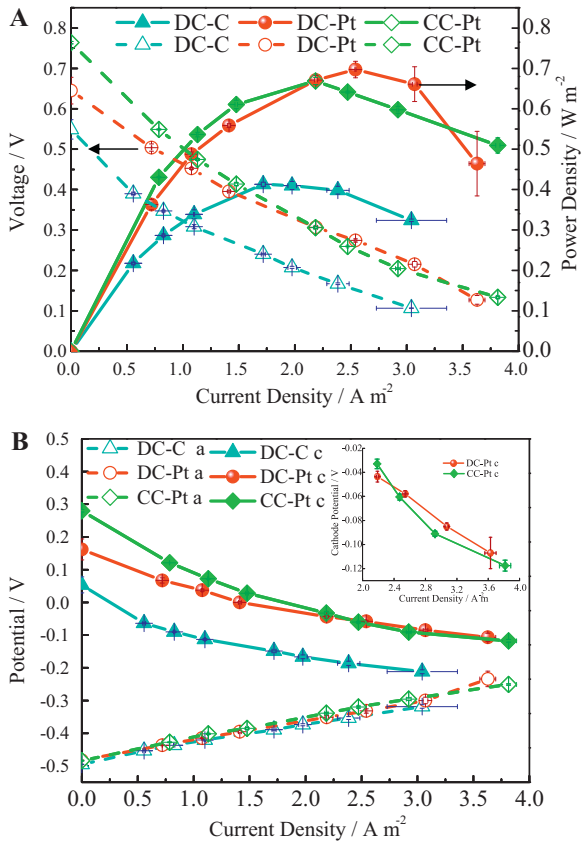

Fig. 2. Power densities (A) and electrode potentials (B) of MFCs using different cathodes (vs. Ag/AgCl, 195 mV vs. SHE). CC-Pt: the carbon cloth cathode with 10% Pt and diffusion layers; DC-Pt: the double-sided cloth cathode with 10% Pt and without diffusion layer; DC-C: the double-sided cloth cathode with carbon powder and without diffusion layer; a, anode; c, cathode. Error bars ± SD were based on averages measured in triplicate.

face matrix was made of hydrophobic polyester fiber coated with a copper layer during fabrication. The inner matrix was composed of hydrophobic polyurethane sponge coated with corrosion-resistance nickel–copper alloy. This alloy had been demonstrated to enhance the resistance to corrosion of stainless steel electrode in previous study [16]. As the alloy of nickel–copper provided excellent conductivity, the surface resistivity of double-sided cloth was only 0.05 $\Omega\,m^{-2}$. Water leakage was prevented due to the hydrophobicity of both the surface and the inner materials mentioned above. Besides, the DC was light weighted (343 $g\,m^{-2}$), excellent in flexibility, surface conductivity and corrosion resistance, making it possible for cathode material.

The results of EDS showed that the surface coating of DC was composed of Cu. Different from the surface elements, the coating of inner matrix was consisted of Ni and Cu with the atom ratio of 1:1. Based on the results of the surface of DC obtained by XRD, the most intense and characteristic diffraction peaks of Cu species appeared at 2θ of 1 1 1 (strongest peak), 2 0 0, 2 2 0 and 3 1 1.

3.2. Performance of MFCs using different cathodes

As shown in Fig. 2A, the maximum power density of MFCs using DC-Pt cathode was $0.70 \pm 0.02\,W\,m^{-2}$, which was similar to that obtained using CC-Pt cathode ($0.66 \pm 0.01\,W\,m^{-2}$). Measurement of the electrode potentials (Fig. 2B) shows that the differences on power production were due to performance of the cathodes and not the anodes, indicating that DC has a comparable or even better performance than CC as cathode material. It should be noted that DC was directly used as cathode without any diffusion layer, while CC cathode was manufactured by painting a PTFE-carbon base layer followed by four PTFE diffusion layers as described previously [6]. Pt can work well with DC without diffusion layer, so did other oxygen reduction catalysts such as CoTMPP and FePc. The maximum power density of 0.76 $W\,m^{-2}$ was obtained using traditional carbon cloth cathode with Pt catalyst (0.5 $mg\,cm^{-2}$) [6], which was similar to that obtained using DC-Pt cathode ($0.70 \pm 0.02\,W\,m^{-2}$). With the same DC matrix, the maximum power density decreased by 38% ($0.41 \pm 0.01\,W\,m^{-2}$) when the catalyst was changed from Pt into carbon powder.

CEs and COD removal rates were obtained when MFCs were stably operated for 30 days. The utilization of DC instead of CC did not change both of the COD removal rates and CEs, with COD removal rates of 75% and CEs of 18 ± 1%. These CEs were similar to those obtained in previous studies using the traditional carbon cloth cathode with four PTFE layers (CE of 20–27%) [6]. The COD removal rates and CEs slightly decreased to 66 ± 2% and 14 ± 1% when the catalyst was carbon powder (DC-C).

3.3. Oxygen permeability of the cathodes

Oxygen mass transfer coefficient (k) of CC-Pt with a carbon based layer and four PTFE layers was calculated as $1.21 \pm 0.05 \times 10^{-3}\,cm\,s^{-1}$, which is comparable with $1.1 \pm 0.1 \times 10^{-3}\,cm\,s^{-1}$ reported by Zhang et al. [10]. However, this result is slightly lower than $2.3 \pm 0.2 \times 10^{-3}\,cm\,s^{-1}$ previously obtained using the same type of cathode [6]. The difference could be due to the differences on batches of the carbon cloth or variations in fabrication procedures by different researchers. The oxygen mass transfer coefficient of DC-Pt cathode was $0.45 \pm 0.03 \times 10^{-3}\,cm\,s^{-1}$, with a value of the same order of magnitude as that of CC-Pt, indicating that DC matrix had the same oxygen diffusivity as CC with diffusion layers. DC-C had a similar k value of $0.44 \pm 0.06 \times 10^{-3}\,cm\,s^{-1}$ as DC-Pt, showing that the oxygen mass transfer coefficient was mainly determined by the electrode matrix, binder, etc., but except the catalyst.

3.4. Cost of cathodes

The cost of the conventional air-cathode matrix, for example carbon cloth, is about 1000$ m^{-2} (BASF, USA), which was a factor of 200 times higher than that of double-sided cloth (5$ m^{-2}). As the preparation of diffusion layer needs carbon powder, PTFE, and solidification process at 370 °C, it was estimated that the manufacture cost of diffusion layers is about 50$ m^{-2}. Since double-sided cloth can be used directly as cathode without diffusion layer, the total cost of cathode can be decreased from 1750$ m^{-2} to 705$ m^{-2} (Pt catalyst), assumed that the price of Pt was 700$ m^{-2}. Carbon powder was demonstrated to be a promising substitute for Pt, with a price around 4$ m^{-2}. When carbon powder was used as the catalyst on the cathode, the total cost of cathode can be further decreased to 9$ m^{-2}, although the maximum power density ($0.41 \pm 0.01\,W\,m^{-2}$) catalyzed by carbon powder decreased by 38% compared to that obtained using Pt ($0.66 \pm 0.01\,W\,m^{-2}$).

Based on the maximum power densities obtained by cubic reactors, the costs of cathodes were recalculated as follows: 2652$ W^{-1} (CC-Pt), 1007$ W^{-1} (DC-Pt) and 22$ W^{-1} (DC-C). It was clearly showed that DC-C was cost-effective, decreased the cost of cathode based on power output by two orders of magnitude.

4. Conclusions

A novel and inexpensive material, double-sided cloth (DC), was used as air-cathode matrix without diffusion layer. Using

Pt as catalyst, the maximum power density of DC cathode was $0.70 \pm 0.02\,W\,m^{-2}$, which was similar to that obtained in MFCs with carbon cloth (CC) cathode. The oxygen mass transfer coefficients of both DC-Pt cathode ($0.45 \pm 0.03 \times 10^{-3}\,cm\,s^{-1}$) and CC-Pt cathode ($1.21 \pm 0.05 \times 10^{-3}\,cm\,s^{-1}$) were of the same order of magnitude, resulting in similar Coulombic efficiencies (CEs) and COD removal rates. When the carbon powder was used as catalyst on DC, the cost based on power output decreased from 2652$ W^{-1} (CC-Pt) to 22$ W^{-1} (DC-C), with a value decreased by two orders of magnitude. These results indicated that the hydrophobic polymer coated with corrosion-resistance alloy, such as DC, was a promising and cost-effective air-cathode material for the enlargement of MFCs.

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