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Anode modification with formic acid: A simple and effective method to improve the power generation of microbial fuel cells

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ABSTRACT

The physicochemical properties of anode material directly affect the anodic biofilm formation and electron transfer, thus are critical for the power generation of microbial fuel cells (MFCs). In this work, carbon cloth anode was modified with formic acid to enhance the power production of MFCs. Formic acid modification of anode increased the maximum power density of a single-chamber air-cathode MFC by 38.1% (from 611.5 ± 6 mW/m^2 to 877.9 ± 5 mW/m^2). The modification generated a cleaner electrode surface and a reduced content of oxygen and nitrogen groups on the anode. The surface changes facilitated bacterial growth on the anode and resulted in an optimized microbial community. Thus, the electron transfer rate on the modified anodes was enhanced remarkably, contributing to a higher power output of MFCs. Anode modification with formic acid could be an effective and simple method for improving the power generation of MFCs. The modification method holds a huge potential for large scale applications and is valuable for the scale-up and commercialization of microbial fuel cells.

1. Introduction

Microbial fuel cells (MFCs) are promising devices that generate electricity from organic wastes using microorganisms as catalysts [1]. The power output of MFCs is inherently limited by the maximum rate of electron transfer that can be sustained by anodic bacteria [1]. Hence the anode material plays a crucial role in the power production of MFCs. Carbon-based materials such as carbon cloth (mesh), carbon paper, carbon felt, activated carbon, graphite fiber brush, and graphite granule [2] have been widely used as the anode material in MFCs, because of their high chemical stability, electrical conductivity, and biocompatibility. Carbon cloth is one of the most promising anode materials for MFCs. The flat-plate configuration enables a reduced electrode spacing, thus a lower internal resistance and higher volumetric power density can be achieved [3].

Modification of the anode surface is an effective approach to increase the power production of MFCs. For instance, treatment of carbon cloth anode with ammonia gas at high temperatures reduced the start up time of a MFC by 50%, and increased the power density from 1640 mW/m^2 to 1970 mW/m^2 [4]. Other effective methods include oxidation of the anode material with acids, addition of conductive polymers and metal oxides, or incorporating with carbon nanotubes [2]. However, these modification methods generally need complicated apparatuses, multiple steps and/or expensive agents. Large scale applications of MFCs for wastewater treatment or bioenergy production require more effective, simple and reliable approaches for modifying the anodes.

The purpose of the present work was to improve the power generation of MFCs by modifying the carbon cloth anode with formic acid. Formic acid (HCOOH) has the chemical properties of both carboxylic acid and aldehyde, so it can react with a wide range of organic and inorganic chemicals [5]. Formic acid has been widely used as a cleaner for various industrial products, such as printed circuit board, steel and toilet bowl [5,6], based on its unique advantages in good dissolving capacity for polar organic matters (such as resins, oils, rosins, and alkanes), relatively low cost, and readily evaporation without leaving any residue. Since surface contamination (e.g. by oils, alkaloids, resins, etc.) during the fabrication process of carbon cloth is inevitable, we expect that formic acid might also be useful in cleaning and purifying the carbon cloth electrode in this study. At present, little information is available in literature about the use of formic acid for treating electrode materials neither in MFCs nor in other fuel cells. The modification was achieved by a simple soaking and air drying process, which has the advantages of low energy cost, simple operation and stable treatment efficiency. Hence the reported method is expected to be feasible for large scale applications.

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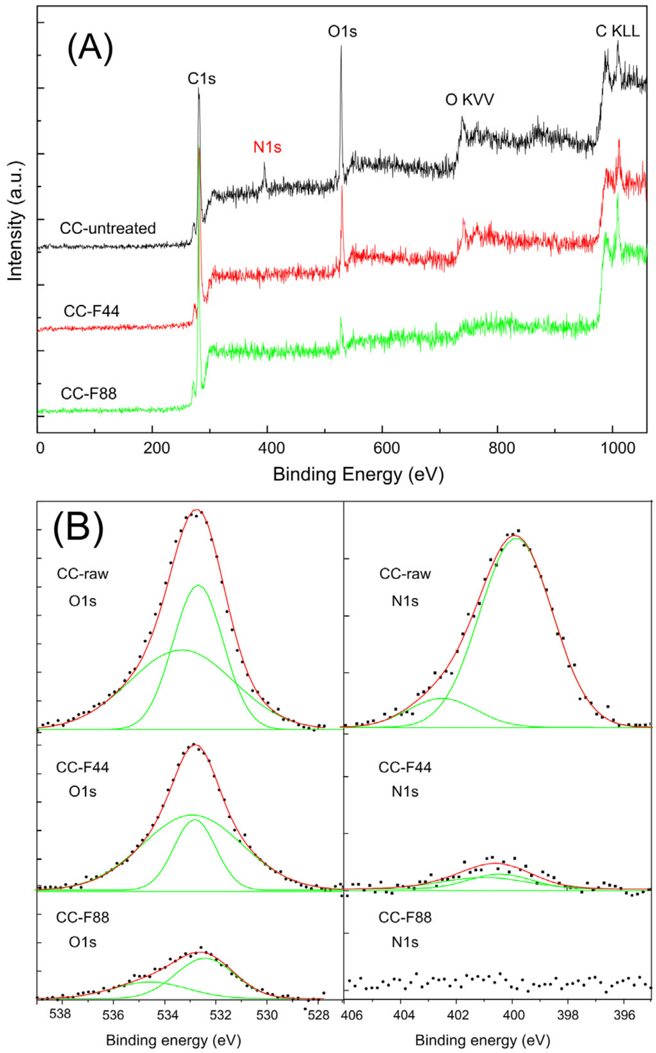

Fig. 1. XPS spectra of the formic acid modified anodes compared to the untreated control: (A) whole spectra, (B) high-resolution spectra of O1s and N1s; baseline substracted.

Table 1
Elemental contents and atomic ratios O/C and N/C of different anodes as determined by XPS.

Anodes	CC-untreated	CC-F44	CC-F88
C (%)	77.78	88.46	95.76
O/C (%)	20.73	11.09	4.34
N/C (%)	7.84	1.96	0.00
O (%)	16.12	9.81	4.24
C—OH and/or C—O—C	7.52	4.48	2.79
Chemisorbed oxygen	8.60	5.33	1.44
N (%)	6.10	1.73	0.00
Pyrrolic/pyridone N	5.34	1.59	0.00
Pyridine-N-oxide	0.76	0.14	0.00

2. Materials and methods

2.1. Anodes preparation and characterization

Carbon cloth (CC; Henghui Woven Carbon Fiber Co., China) was used as the anode material for MFCs. The raw cloth was cleaned with distilled water, dried and cut into circles of 4 cm in diameter to form the untreated anode (denoted as CC-untreated). For formic acid modification, the untreated anode was soaked into 5 mL of formic acid solution (mass fraction of 44% or 88%) for 12 h. Then it was rinsed 5 times with distilled water and dried at 100 °C for 4 h in air atmosphere. The product was referred to as CC-F44 or CC-F88, with 44 and 88 representing the formic acid concentration of 44% and 88%.

The elemental composition of the anode materials was evaluated using X-ray photoelectron spectroscopy (XPS; ESCALAB, MARK II, VG, UK) with an Mg Kα X-ray source. All binding energies were referenced to the C 1s peak at 284.6 eV to compensate for the surface charging effects. Relative atomic contents were calculated from the ratio of the peak areas after correcting with the theoretical sensitivity factors. The surface morphology of the different anodes before inoculation, and after 7 days and 3 months of MFC operation was examined using a field emission scanning electron microscope (SEM; Utral 55, CorlzeisD, Germany).

2.2. MFC setup and operation

Air-cathode cubic-shaped MFCs with a cylindrical chamber (reactor volume 14 mL, electrode spacing 2 cm) were constructed as previously described [4]. The air-cathodes were made of nickel foams containing an activated carbon catalyst [7]. MFCs were inoculated with the effluent of a MFC reactor that had been operated for over 3 months. Reactors were fed a nutrient medium containing 1.0 g/L sodium acetate and 50 mM phosphate buffer solution (PBS, pH 7.0; $Na_2HPO_4 \cdot 12H_2O$ 11.47 g/L, $NaH_2PO_4 \cdot 2H_2O$ 2.75 g/L, NH_4Cl 0.31 g/L, KCl 0.13 g/L, trace minerals 12.5 mL/L) as previously reported [4]. The MFCs were operated in a fed-batch mode for 30 days at an external resistance of 1000 Ω, followed by being operated for 60 days at 100 Ω to allow biofilm maturation [8]. All the tests were performed in duplicate in a 30 °C temperature-controlled room.

2.3. Electrochemical analyses

Electrochemical tests were conducted after nearly three months of MFC operation when the anodic biofilms were considered near matured. The polarization and power density curves were obtained by varying the external resistance from 1000 Ω to 50 Ω, with reactors running for 20 min at each resistance. Cyclic voltammetry (CV) was performed on an electrochemical analyzer (CompactStat.e, Ivium Technologies B.V., The Netherlands) at a scan rate of 10 mV/s. A standard three-electrode configuration was used for all measurements, with the anode severing as the working electrode, the cathode as the counter electrode and an Ag/AgCl electrode as the reference electrode. The Ag/AgCl reference was placed in close proximity to the anode. CV curves of the anodes before inoculation and after biofilm maturation were recorded in 50 mM phosphate buffer solution (PBS) with or without 1.0 g/L sodium acetate. In order to exclude the influence of suspended microorganisms on CV results, the nutrient medium of MFCs that contained suspended microorganisms was gently poured out from MFCs and then the MFCs were flushed with PBS. Afterwards, the previous PBS was replaced with fresh PBS or PBS+ sodium acetate for the final CV tests.

3. Results and discussion

3.1. Effect of formic acid treatment on the physicochemical properties of anode

XPS analysis indicated the presence of only C, O and N atoms on the surface of all anodes (Fig. 1A). The untreated anode possessed a high O (16.12%) and N (6.10%) contents on the surface, which probably arose from the surface contaminants (such as oils,