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Deposition of Iron on Graphite Felts by Thermal Decomposition of $Fe(CO)_5$ for Anodic Modification of Microbial Fuel Cells

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In this paper, a new efficient anodic modification method for microbial fuel cells (MFCs) was developed. Fe was deposited on graphite felt by thermo decomposition of $Fe(CO)_5$ and then oxidized to Fe(III) oxides. Fe(Ⅲ) oxides were proved Fe_2O_3 and FeOOH. The unmodified and Fe modified graphite felts were utilized as anode in MFCs. Fe(Ⅲ) oxides on anode promoted the power generation of MFCs. The maximum power density of $18 W/m^3$ and the internal resistance of 51Ω were obtained by the MFC with Fe modified anode, which was significantly superior to the performance of the MFC with unmodified anode. The electrochemical activity and attached bacterial density of Fe modified graphite felts were significantly higher than those of the unmodified graphite felts. This new method for anodic preparation promoted power generation, replaced manual brushing and Nafion solution, and reduced the cost.

Keywords: Iron pentacarbonyl; Thermal decomposition; Anodic modification; Microbial fuel cells; Power promotion

1. INTRODUCTION

Microbial fuel cells (MFCs) have drawn global attention in recent years with the property of direct conversion of chemical energy into electrical energy by exoelectrogenic bacteria attached on the anode [1-3]. Thus, MFCs provide various new opportunities for wastewater treatment and power generation. To date, lots of efforts have been exerted to promote the performance of MFCs [4, 5]. However, the poor power density, low electron transfer efficiency and high construction cost limit the further application of MFCs [6, 7].

In order to improve the performance of MFCs, multiple approaches for anode modification have been employed, such as ammonia treatment [8], electrochemical treatment [9, 10], metal oxide doping [11, 12], and polymer modification [13]. Anodic microbes degrade organic matters and release electrons to anode surface, which depends on a complex system of parameters [14-17]. As a result, anodic materials and modifications greatly influence the performance of MFCs.

Iron possesses fine performance as one of promising approaches for anodic modification of MFCs, such as improving bacterial adhesion [18], electron transfer and capacitance behavior [12]. Moreover, traditional methods of electrode modification depend on the means of brushing catalysts manually on electrodes with activated carbon powder or carbon nanotubes doped [13, 19, 20], which is low-effective and susceptible to individuals. For the purpose of promoting MFCs into practical application as soon as possible, the impact of artificial factors on the process of electrode preparation should be decreased to the greatest degree. As a result, new industrialized methods must be explored to replace traditional methods of modification. In addition, in traditional modification, the use of Nafion solution as the binding agent for electrodes is indispensable [6, 21]. The high price of Nafion solution substantially increase construction cost of MFCs.

In this paper, Fe was deposited on the graphite felt by thermo decomposition of $Fe(CO)_5$. $Fe(CO)_5$ is in liquid state at room temperature, in gaseous state at 103℃ and decomposes into Fe and CO at 160℃ [22]. We utilized the property of state convert and thermal decomposition of $Fe(CO)_5$ at relatively low temperature range to construct a reactor for electrodes preparation. $Fe(CO)_5$ was released in the reactor in liquid state and evaporated to gaseous stated after being heated. Gaseous $Fe(CO)_5$ filled the reactor, as well as the internal space of graphite felt. Then $Fe(CO)_5$ was decomposed on the surface of heated graphite felt as soon as the temperature reached 160℃.And iron could be deposited on the internal graphite felt fibers and the surface morphology of iron was uniform. Then elemental Fe on graphite felts was oxidized to Fe(Ⅲ) oxides. Afterwards, an air-cathode membrane-less single-chamber MFC was constructed to test the performance of MFCs with Fe modified anode. In comparison with the MFC with unmodified anode, Fe modified MFC showed higher electrochemical activity, anodic bacterial density and power generation.

2. MATERIALS AND METHODS

2.1 Deposition of Fe on graphite felt

A sealed reactor made of glass was constructed for deposition of iron on graphite felt by thermal decomposition of $Fe(CO)_5$ (Figure 1A). A piece of 5mm thick graphite felt (26.5 × 5cm, about 0.5Ω) (Sanye Carbon Co., Ltd, Beijing), was placed in the center of the reactor as a resistor and connected to a DC power supply (TPR3030D, 30V, 30A) (Longwei Instruments Co., Ltd, Hong Kong). The temperature at the surface of the graphite felt was detected by a mercury thermometer. A syringe was installed on the top of the reactor and its long needle punctured through the graphite felt to the bottom. The gas inlet pipe and gas outlet pipe were set at the left and right side of the reactor, respectively.

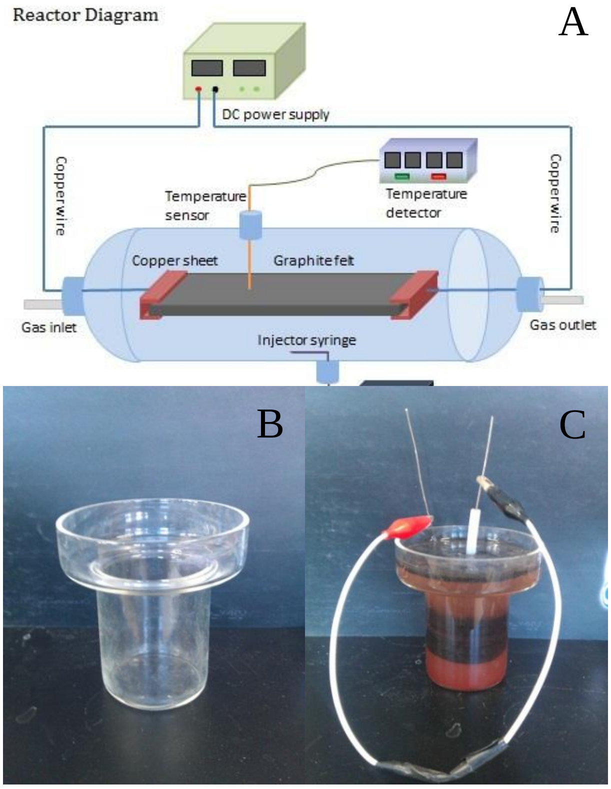


Figure 1. Reactor of deposition of Fe on graphite felt (A) and construction of MFC reactor (B) (C).

The reactor was assembled as above, and a certain volume of liquid $Fe(CO)_5$ was in syringe beforehand. After a 5 minutes N_2 purge, the DC power supply was turned on to heat the graphite felt. $Fe(CO)_5$ was released to the bottom of reactor when the temperature of graphite felt was heated to 100℃. $Fe(CO)_5$ was kept in liquid state at the beginning and then evaporated to gaseous state due to the thermal diffusion from heated graphite felt. $Fe(CO)_5$ started to decompose when the temperature of graphite felt reached 160℃, and the temperature was kept at 165℃ to 175℃ for 3min to ensure the complete decomposition of $Fe(CO)_5$ (The current of DC power supply was about 15-17A at the temperature). Then, DC power supply was turned off and N_2 was re-ventilated to remove the CO in the reactor till the temperature of graphite felt dropped to room temperature.

In this experiment, 10μL of $Fe(CO)_5$ (2.2mg Fe included)was released into the reactor to prepare Fe modified anode. The same graphite felt was operated to prepare unmodified anode for comparison as the procedure mentioned above without the addition of $Fe(CO)_5$.

2.2 Microbial fuel cells setup

The diagram of the single-chamber membrane-less MFCs used in this research was shown in Fig 1B. The bottom anode chamber is cylindrical with 6 cm in height and 4.2 cm in diameter and the upper cylindrical cathode chamber exposed to air is 2 cm in height and 7.6 cm in diameter. The rectangular graphite felt getting from the reactor after thermal decomposition of $Fe(CO)_5$ was cut into

5 pieces as anode, each 4cm in diameter. Meanwhile, the cathode was a piece of Pt coated ($0.3mg/cm^2$) graphite felt with 3mm thick and 7.5cm in diameter. Titanium wire was used for the connection of the external circuit to the electrodes.

MFCs were inoculated with a mixed bacterial culture from other MFCs that was originally inoculated with primary clarifier overflow from Gaobeidian Wastewater Treatment Plant in Beijing and had been running for more than two years [9]. MFCs were fed with a medium containing 50mM Sodium acetate in 50mM phosphate buffer solution (Na_2HPO_4, 4.09g/L and $NaH_2PO_4 \cdot H2O$, 2.93g/L)[23, 24], NH_4Cl (0.31g/L), KCl (0.13g/L), metal salt (12.5mL/L) and vitamin (5mL/L) solutions and re-fed with 50Mm Sodium acetate every three days. MFCs were operated in fed-batch mode at a fixed external resistance of 500Ω (except as indicated). As shown in Figure 1C, the anode were immersed in the mixed solution as mentioned above, and one side of the cathode was in contact with the solution and the other side, exposed to the air. All tests were operated at 25℃.

Iron coating on graphite felt was oxidized to Fe(III) oxides in contact with the electrolyte in MFCs. And during this process, current was generated since iron on anode transferred electrons to cathode through the external circuit. For the comparison of power generation and anodic catalytic performance with unmodified MFC, the effect of power generation due to the oxidation iron was eliminated by continuous aeration (for accelerating the oxidation of iron) in anodic chamber before inoculation until the current of the MFC dropped to baseline (the voltage output was under 10 mV). The iron on anode could be supposed oxidized completely at the time. Then the MFC with Fe modified anode was inoculated with the mixed bacterial culture as mentioned above.

2.3 Analyses and calculations

Cell voltages were measured every 20 minutes using a data acquisition system (AD8251H, Ribohua Co., Ltd, Beijing). The current density and the power density were both normalized to the volume of anode chamber. Internal resistance was calculated by polarization slope method by varying the external resistance.

Electrochemical activity of anodic graphite felts was measured by Cyclic Voltammetry (CV) (CHI660D, Chenhua Instruments Co., Ltd, Shanghai). The anode with and without inoculation were cut into quadrate pieces (1cm*1cm). And these anodic pieces was rinsed with DI water and assembled in a three electrode electrochemical cell filled with the electrolyte (phosphate buffer, pH 7.0, 0.2M). The electrolyte was purged with Argon before the electrochemical measurements started. A saturated calomel electrode (SCE) was used as reference electrode during the tests.

The anodic surface morphologies were examined by thermal field emission scanning electron microscopy (TFE-SEM) (JSM-7001F, JOEL) and environmental scanning electron microscopy (ESEM) (Quanta 2000, FEI) respectively. And the valence and compound composition were examined by Fourier transform infrared spectroscopy (FT-IR) (ALPHA，Bruker Optics) and X-ray photoelectron spectroscopy (XPS) (Microlab MK Ⅱ，VG Instruments). Before the tests, the graphite felts from anode were rinsed with buffer (pH 7.0, 0.2M) and DI water and dried in vacuum drying oven at 60℃ for 24 hours. And graphite felts were ground into powder before FT-IR and XPS tests.

3. RESULTS AND DISCUSSIONS

3.1 FT-IR and XPS studies

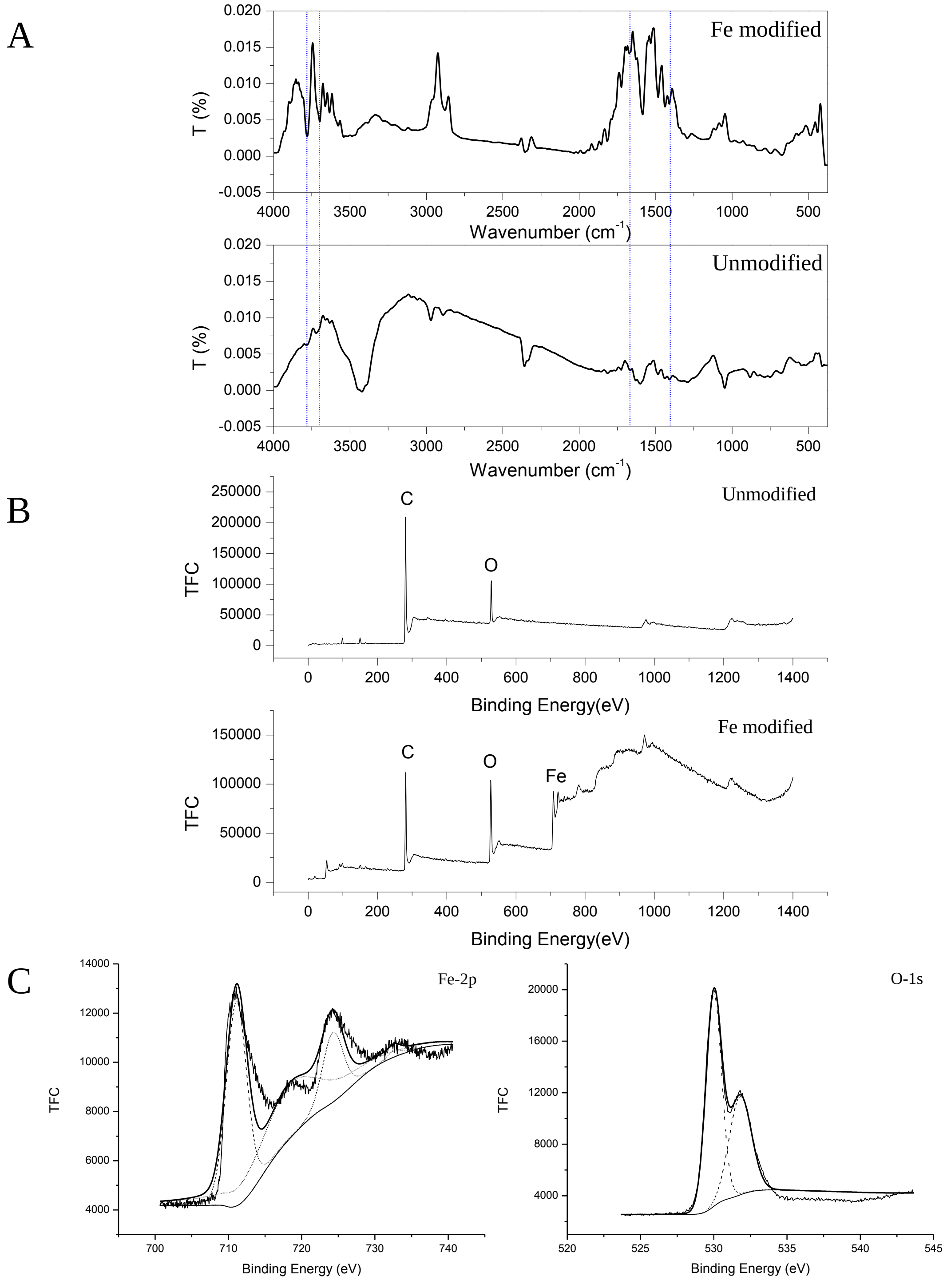


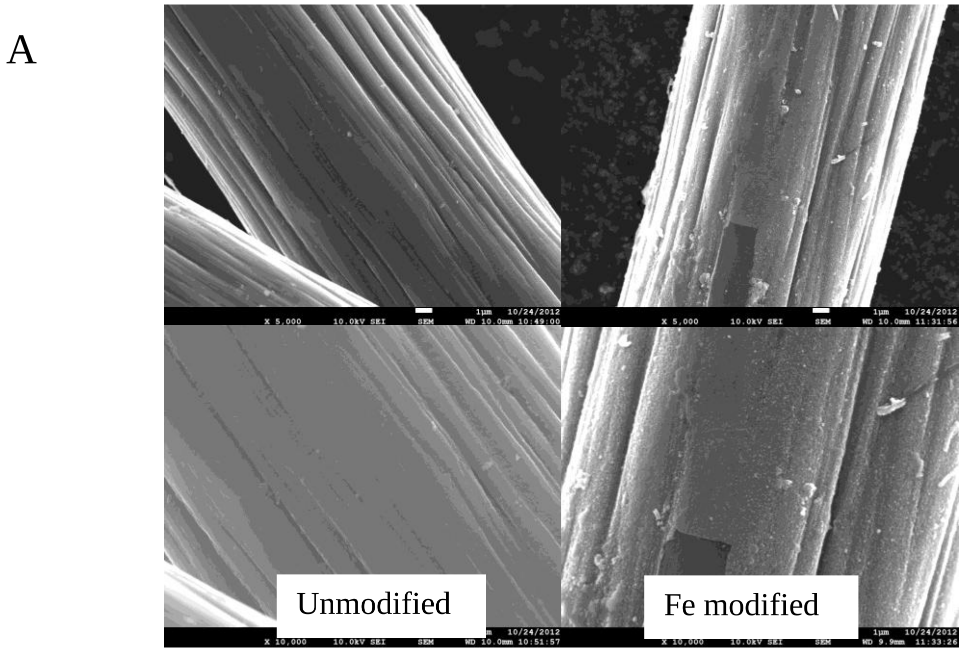
Figure 2. FT-IR spectra (A) and XPS spectra (B) of unmodified and Fe modified graphite felts, and Fe-2p and O-1s XPS spectra of Fe modified graphite felt (C).

FT-IR was employed to investigate functional groups on anodic graphite felts and the FT-IR spectra of unmodified and Fe modified graphite felts were compared (Figure 2A). The absorption bands in the range 3800-3600 cm^{-1} indicated the characteristics of OH^{-1} ions and the bands at 1651 cm^{-1} and 1388 cm^{-1} represented the Fe-O vibrational mode[25, 26].

The elements and valence of iron compounds on anodic graphite felts were detected by XPS. In Figure 2B, the XPS spectra of unmodified and unmodified graphite felts were compared, a distinct difference between the two spectra indicated the existence of iron [27]. And then, the XPS spectra of Fe modified anode was analyzed to investigate further the valence and composition. As Figure 3C shown, the peak in Fe-2p XPS spectra certified Fe_2O_3 at 711.1 eV and FeOOH at 724.2 eV respectively. Meanwhile, the peak in C-1s XPS spectra demonstrated Fe_2O_3 at 530.0 eV and FeOOH at 531.8 eV respectively. Then, after multiple peaks fitting shown in Figure 3C, the mass ratio of Fe_2O_3/FeOOH was 2.8 in Fe-2p XPS spectra by calculating the peak areas. We confirmed the composition of the iron compounds was the mixture of Fe_2O_3 and FeOOH [28-31]. Via the XPS studies, it came to a conclusion that iron deposited on graphite felts turned to Fe_2O_3 and FeOOH under the effect of electrolyte solution.

3.2 Anodic SEM studies

SEM was employed to study the surface morphology before inoculation and the bacterial morphology and density after inoculation of unmodified and Fe modified graphite felts. As shown in Figure 3A, the graphite fiber from unmodified graphite felts was smooth, while the fiber from Fe modified graphite felts was obviously covered and the surface morphology of iron coverage was much rougher.



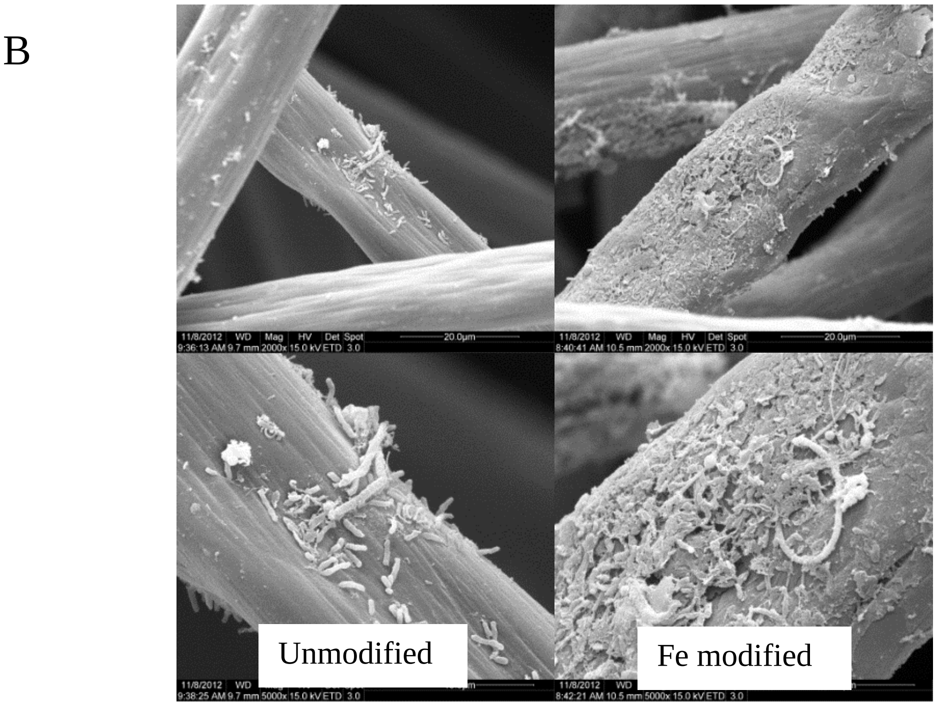


Figure 3. SEM images of unmodified and Fe modified graphite felts before inoculation (A) and after inoculation (B).

The coverage of iron on graphite fiber could be seen generally uniform from the exposed bare fiber and iron coverage faultage. Compared with manual brushing for electrode modification, the Fe modified surface was more homogeneous because graphite felt fibers were evenly heat during the anodic preparation and the Fe was deposited onto the graphite fiber surface during $Fe(CO)_5$ decomposition.The bacterial morphology and density on graphite felts examined by SEM reflected the performance of anodic catalyst. As shown in Figure 3B, the density of bacterial adhesion on Fe modified graphite felts was significantly higher than that on unmodified ones, which very likely due to the rough surface resulting in the increase of surface area. In addition, previous studies reported that iron affected the biofilm development and electron transfer property and Fe(Ⅲ) oxides promote the bacterial adhesion and biofilm formation. The results demonstrated that Fe(Ⅲ) oxides increased anodic bacterial adhesion.

3.3 Cyclic voltammetry studies

Figure 4 showed the cyclic voltammograms of unmodified, Fe modified graphite felts before and after inoculation. No distinct peak was observed from the CV curve of the unmodified graphite felts so the unmodified fresh graphite felt was inert and without redox activity. And a strong oxidation peak appeared from the CV curve of Fe modified graphite felts. According to the standard oxidation reduction potential (pH = 7) of some ferric ions and oxides ($FeOOH/Fe^{2+}$ -0.274 V, Fe_2O_3/Fe^{2+} -0.287

V)[32], the strong oxidation peak between +0.2 to +0.3 V in CV curves proved the existence of Fe(III) oxides and the result was in great agreement with the conclusion obtained by FT-IR and XPS studies.

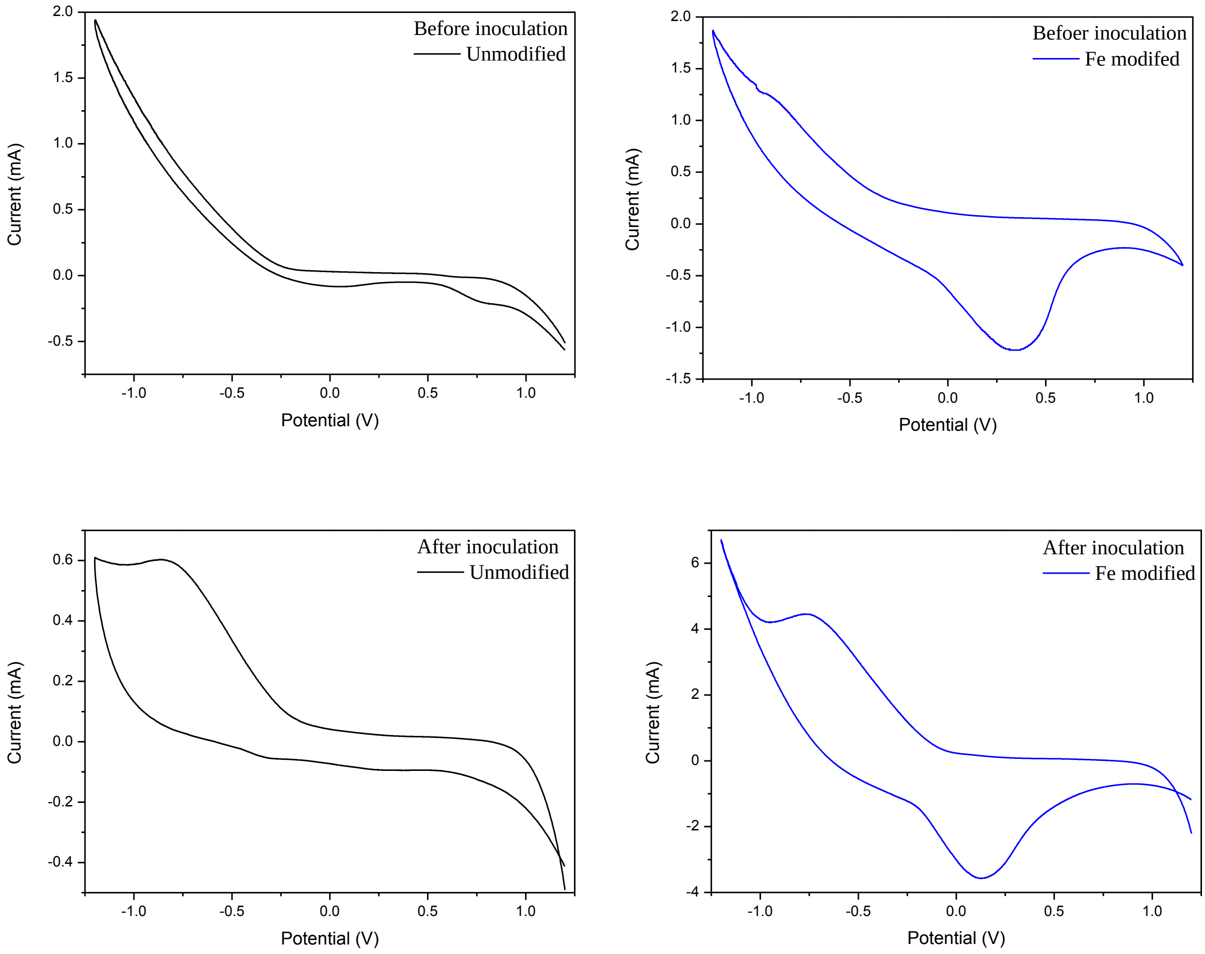


Figure 4. Cyclic voltammograms of unmodified, Fe modified graphite felts before and after inoculation (Scan rate = 25mV/s).

In addition, the peak current and area of Fe modified graphite felts with and without inoculation were much larger than those of unmodified ones, which indicated that electrochemical activity of Fe modified graphite felts was much higher than that of the unmodified graphite felts.

3.4 MFCs performance

Figure 5 showed the voltage output curves (A) and power density curves (B) of MFCs with unmodified and Fe modified anode. As shown in Figure 5A, the maximum voltage output of the MFC with Fe modified anode was 580 mV, around 40% higher than the maximum voltage output of MFC with unmodified anode (422 mV). The comparative results of polarization curves and power density curves between unmodified and Fe modified MFCs was obviously distinct as shown in Figure 5B.

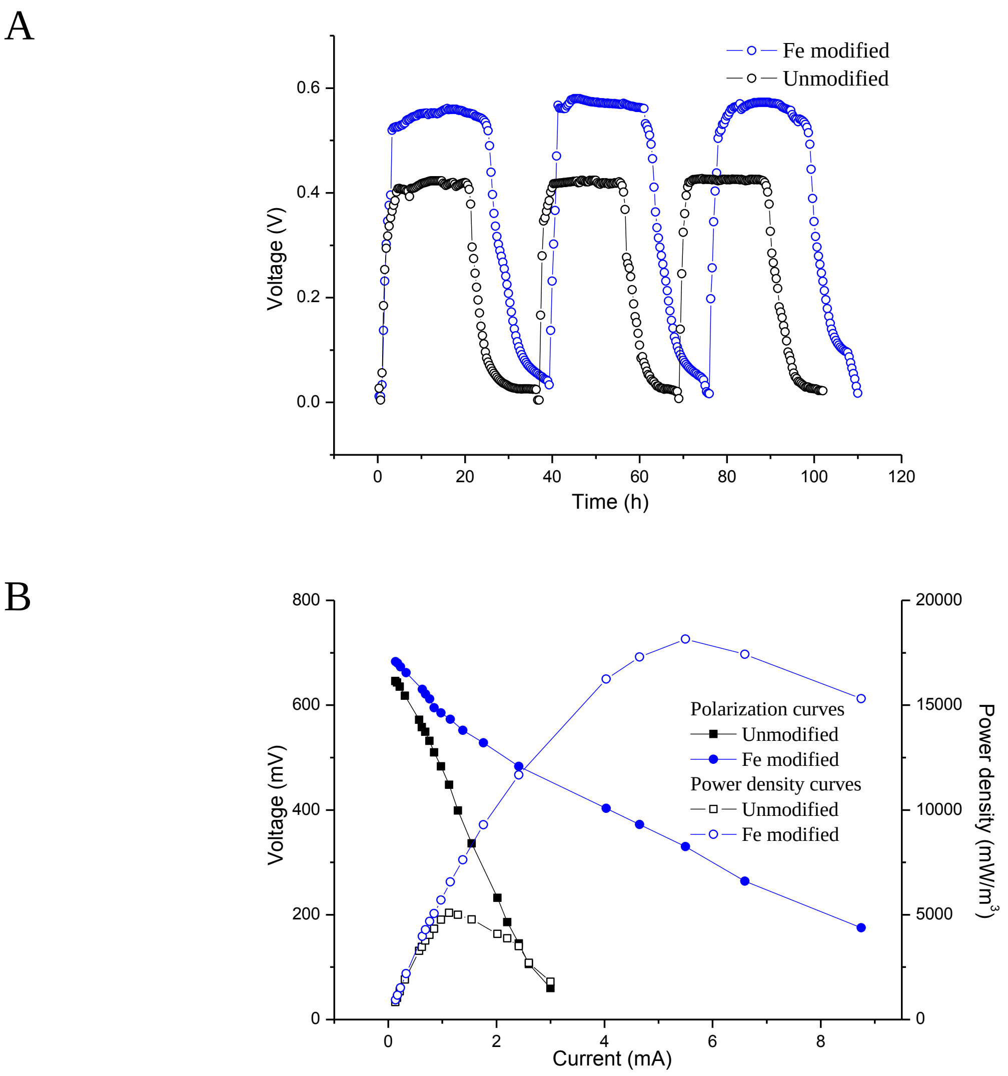


Figure 5. Voltage output curves (A) and polarization and power density curves (B) of MFCs with unmodified, Fe modified anode.

The internal resistance of unmodified and Fe modified MFCs were 188 Ω and 51 Ω respectively by calculating the slope of polarization curves. And maximum power densities of unmodified and Fe modified MFCs obtained from curves were 5 W/m^3 and 18 W/m^3 respectively. The internal resistance and power density of MFC with Fe modified anode were respectively 72% lower and 260% higher than those of MFC with unmodified anode.

Previous researches reported that the electrons shuttle to anode surface involved Fe(III) in cytochromes [12, 33-36] and the use of iron oxide-coated electrode had improved the power density. From the comparison of power generation performance, the conclusion we got was that Fe(III) oxides on anode promoted power generation and decreased internal resistance of MFCs.

4. CONCLUSION

Fe was deposited on graphite felts of MFCs by thermal decomposition of $Fe(CO)_5$ and oxidized to Fe_2O_3 and FeOOH. Fe_2O_3 and FeOOH on anode elevated the electrochemical activity, improved the bacterial adhesion and enhanced the power generation. The maximum power density and the internal resistance of MFC with Fe modified anode obtained were 18 W/m^3 and 51Ω, which were 72% lower and 260% higher than those of MFC with unmodified anode respectively. The new method for anodic preparation of MFCs reduced the cost of construction and simplified the procedure of anodic preparation compared with previous anodic catalyst and preparation.

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