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Research Article

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Reaction mechanism on anode filled with activated carbon in microbial fuel cell

YU Jin

Shenyang Jianzhu University, China

ABSTRACT

The upflow microbial fuel cell （MFC） system with membrane-free air-cathode was developed, and landfill leachate as fuel. The anode was made of stainless steel mesh filled with activated carbon， and carbon felt as the cathode. Electricity production performance of MFC with cylindrical stainless steel mesh anode filled with 0 (unfilled), 1mm, and 3mm cylindrical activated carbon particles was investigated. The electrochemical process of anode was observed by the cyclic voltammetry test. The mechanism of anode electrode reaction was analyzed. The results showed that the electricity generation performance of MFC with the anode filled with activated carbon was better than that of unfilled MFC. Maximum volumetric density of 4056.4mW/m^3 and the apparent internal resistance of 494Ω were achieved from MFC with anode filled with 1mm particle. With the decrease of filled particles size (anode surface area increase), the electrochemical activity of microbes enriched on the surface of graphite rod increased. The electrode reaction process of anode with unfilled and filled with 1mm and 3mm particle were an irreversible process, a reversible process and a partially reversible process.

Key words: MFC; Cyclic voltammetry test; Stainless steel mesh anode; peak current.

INTRODUCTION

Research on microbial fuel cells (MFCs) has at present drawn increasing attention in the past decade due to an increased concern about the global energy crisis and the technology can directly convert mixed organic substrates to electricity using bacteria as a biocatalyst. At present, a number of experiments mainly focused on the effect of medium, electricity producing bacterium, battery configuration and the electrode material on the electricity generation performance of MFC. Although MFCs promise sustainable energy generation in the future, many major bottlenecks still exist [1], such as the characteristic, mechanism and electrode kinetic processes of the electrode reaction. As one method of the important electrochemical qualitative analyses, cyclic voltammetry test is an important device for study the election reaction. Xu Wei [2] investigated the different phase within an electricity-generating cycle and whole discharge process of sedimentary MFC with graphite cloth anode and the glucose as fuel by the cyclic voltammetry method. A presence of redox peak at approximate-0.4 V (versus saturated calomel electrode), and the height of peak in voltammogram was found to change with the electricity-generationg process in MFCs. The characteristic of the production of compounds with electrochemical activity and the variation of amount of these metabolic products in the anode chamber was investigated. Guo Kun etal [3] investigated the behavior of microbial enriched on the surface of graphite rod of short arm type air cathode MFC by the cyclic voltammetry method, and they found that these enriched microbial has electrochemical activity. DU Zhuwei[4] compared the behavior of anode enriching and unenriching microbial by the cyclic voltammetry method. The cyclic voltammetry results showed the anode enriching microbial has redox peaks, but unenriching microbial has no peak, which indicates that anode enriching microbial has a higher electrochemical activity. Navanietha etal [5] modified electrode by electrochemical deposition in order to improved performance of microbial fuel cells and the electrocatalytic activity of the biofilm growing on the anode were characterized by cyclic voltammetry. They found the performance improved by 20.75% when compared to the bare electrode. Rabaey, K etal [6] investigated the performance of microbial fuel cells operated in a continuous mode. Cyclic voltammetry was performed to determine the potential of the in-situ synthesized bacterial redox mediators. Catalytic activity of Manganese cobaltite nanorods (MnCo2O4 NRs) prepared as potential air-cathode catalyst for the single-chambered microbial fuel cells (sMFC) by the cyclic voltammetry, linear sweep voltammetry and electrochemical impedance [7].Lu Min etal.[8] investigated electrocatalytic activities of three types of manganese dioxide as alternative cathode catalysts in air-cathode microbial fuel cells by cyclic voltammetry (CV).In this experiment upflow MFC system with membrane-free air-cathode was consisted, stainless steel mesh filled with cylindrical activated carbon particles as anode, carbon felt loaded Fe / C catalyst as cathode and landfill leachate as fuel. The effect of the stainless steel mesh anode filled with different cylindrical activated carbon on electricity generation performance of MFC was investigated. Electrochemical behavior and electrode reaction process were analyzed on the basis of cyclic voltammetry results with different scan rates.

EXPERIMENTAL SECTION

A. Electrode preparation

Stainless steel mesh was rolled into a cylinder with 1cm diameter to make the anode. One anode was no filled and the other two anodes were filled with 1mm and 3mm cylindrical activated carbon particles. Put the prepared anode in anaerobic granular sludge containing landfill leachate to attach microbial and last one month.

Materials for cathode preparation are carbon felt loaded 0.25mol/L Fe $(NO_3)_3$ and 1g activated carbon powder in this paper [9].

B. operation condition

Anaerobic sludge from UASB reactor was used to inoculate the MFC device [6]. Landfill leachate was taken from Shenyang Laohuchong Landfill. Landfill leachate fed into the MFC was diluted and the COD of diluted landfill leachate is about 700mg/L. MFC run continuous with the feeding speed of 45 ml/h and control the temperature at （24±1）℃.

C. Analysis and calculation method

The apparent internal resistance of MFC was determined by the steady-state discharge [10-11]. The voltage was measured using UT71A intelligent digital multimeter. The range of load resistance is 90000-10 Ω. The power density P (mW • m^{-3}) was calculated by the equation of $P = \frac{U^2}{RV}$, where U is voltage (V), R is resistance (Ω), and *V* is effective volume (m^3).

Electrochemical behavior and electrode reaction process of anode were characterized by cyclic voltammetry. Potential scan range for unfilled and filled electrode are respectively -1.05 ~ 0.1V and -0.86 ~ 0.1V, the sensitivity is 100mv.

RESULTS AND DISCUSSION

A. The effect of particle size of filling granularity on MFC electricity performance External resistor of battery changed from 10Ω to 90000Ω, measure the voltage values, polarization curve and power density curves of stabled MFC, the results are showed in figure 3.1. The maximum power density is 4056.4mW/m^3, apparent internal resistance is 494Ω.

Figure 3.1 show the electricity production performance of MFC with filled anode is better than that unfilled and filled 1mm particle is better than that filled 3mm particle. The maximum power density of MFC unfilled, filled with 1mm and 3mm particle is respectively 1915.5mW/m3, 4056.4mW/m3 and 3682.4mW/m3, the apparent internal resistance is respectively 1501Ω, 494Ω, 666Ω. Filling particle can increase the area bacteria attached to, which greatly improved MFC performance. The smaller the filled particle, the greater the surface area of particle, thus the amount of attached bacteria is more and more, which is benefit to electron transfer, reducing the battery's internal resistance and increase the output power.

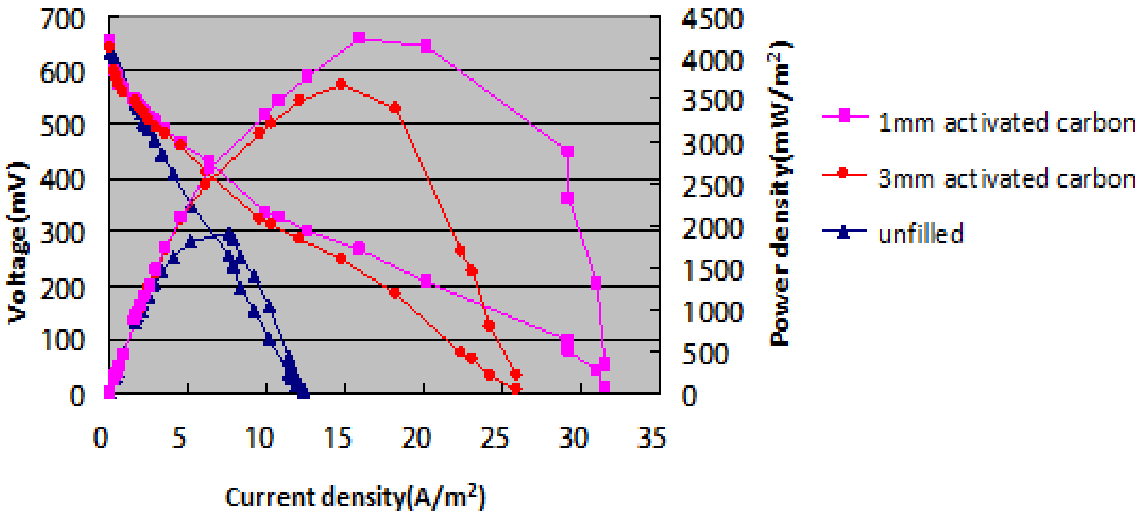

Figure 3.1 The effect of particle size on MFC performance

B. Electrochemical behavior of anode

Cyclic voltammetry is one of the important means to study electrochemical behavior; the cyclic voltammetry test of each anode is showed in figure 3.2. In the same scanning speed each battery will be scanned 20 laps after the battery has been stabilized, the cyclic voltammetrys are almost invariant and have good repeatability. Figure 3.2 shows the different anode cyclic voltammograms tested in the same scan speed of 100mv/s. It can be seen from the figure, three kinds of anode all appear redox peaks, cyclic voltammogram of anode filled with 1mm particle has two small reduction peaks. It show selectrochemical reaction happened on all three electrode, and electrochemical activity is strong. When the particle size is 1mm, the oxidation peak current and reduction peak current reaches the maximum, indicating that the bacteria adsorbed on anode surface has greater electrochemical activity. The greater the peak potential difference, the worse the electrode reaction reversibility. In the same scanning speed, the greater the peak current is, the higher electrochemical activity of the electrode can be got. It can be seen from figure 3.2, when fill the 1mm particle, the peak potential difference is the minimum and the peak current is the maximum, indicating the reversibility of battery is the best, the electrochemical activity is the strongest.

C. The study of anode electrode reaction process

In cyclic voltammetry test, one important mean of study electrode reaction process is scanning speed of the electrode potential and current. The ratio of oxidation peak current and reduction peak current is another important condition to judge whether the electrode process is reversible. Therefore, this paper study the anode electrode reaction process from the scanning speed and the radio of oxidation peak current and reduction peak current.

In this paper, cyclic voltammograms for anode filled with different size cylindrical activated carbon test are showed in figure 3.3, figure 3.4 and figure 3.5 in the scanning speed of 20, 50,100,120,150 mv/s.

In figure 3.3, with the increase of scanning speed, the absolute value of the oxidation and reduction peaks current of anode were increased, but the reduction peak current increased higher. It shows the reducing of anode is better than oxidizing. But the potential values of oxidation peak and reduction peak were almost invariant.

In figure 3.4, oxidation peak and reduction peak appear in pairs, the peak currents are approximately equal, increase with the increase of scan speed, and have no lateral variation. It shows quasi-reversible electrochemical reaction happened in anode, the electrode process can be cyclic oxidation and reduction, makes the reaction to continue. When the scanning speed is 100mV/s, its oxidation potential and reduction potential is respectively -448 and -397 mV, the peak potential differences is 51 mV, the peak potential difference smaller the reversible better, it shows battery materials’ oxidation-reduction reaction reversibility is much better.

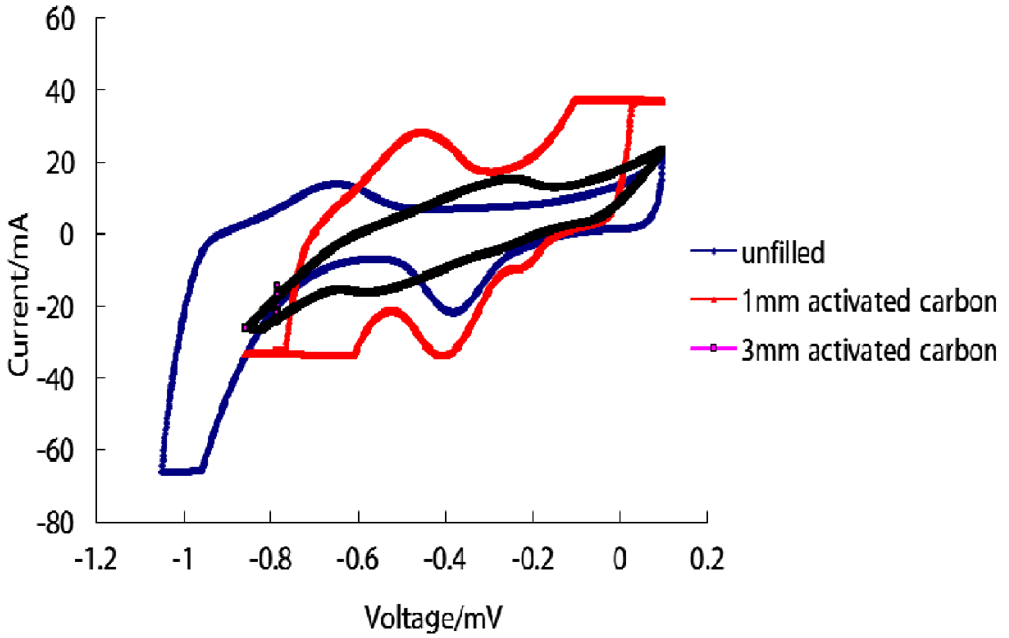

Figure 3.2 Cyclic voltammetry of different anode in the same scanning speed

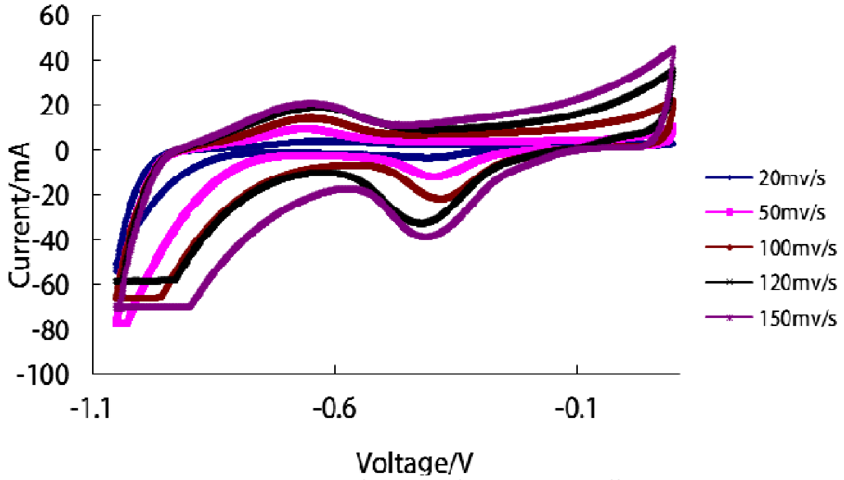

Figure 3.3 Cyclic voltammograms of anode unfilled tested in different scanning speed

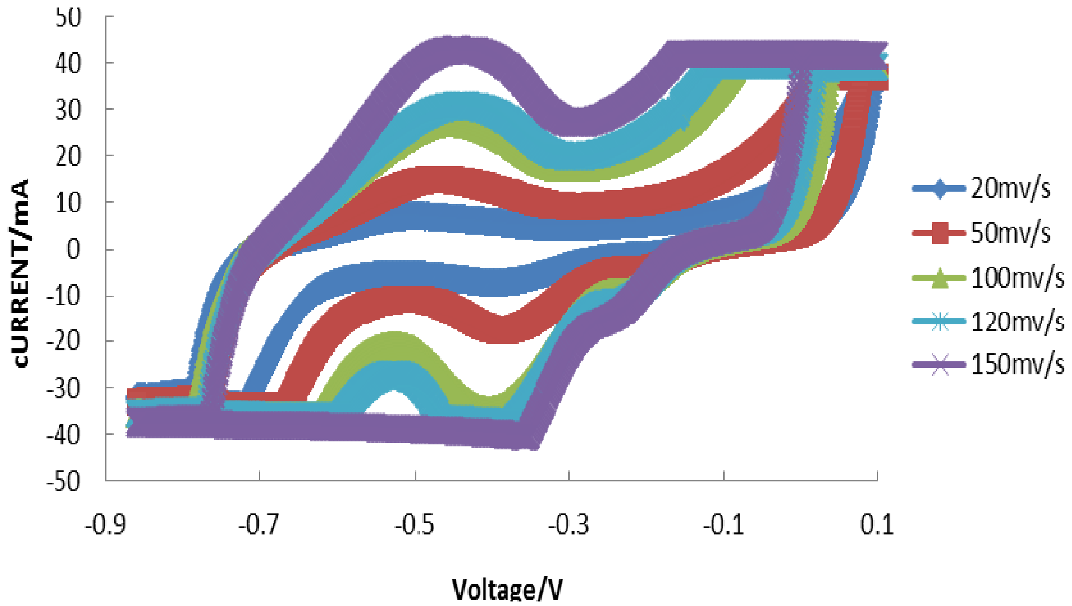

Figure 3.4 Cyclic voltammograms of anode filled with 1mm cylindrical activated carbon tested in different scanning speed

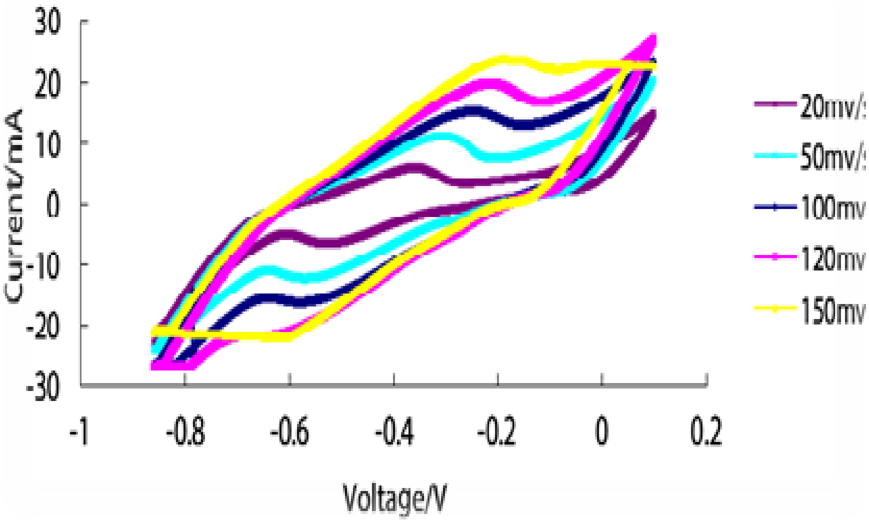

Figure 3.5 Cyclic voltammograms of anode filled with 3mm cylindrical activated carbon tested in different scanning speed

In figure 3.5, the current of oxidation peak and reduction peak increase with the increase of scanning speed, but has lateral variation. It shows oxidation process and reduction process become easier, battery electricity production performance has been improved.

The radio of oxidation peak current and reduction peak current is another important condition to judge whether the electrode process is reversible. Table 3.1 shows the oxidation peak potential, reduction peak potential and their radio were tested in CV with different anodes and different scanning rates.

It can be seen from table 3.1, the oxidation peak potential and the reduction peak current appeared in the negative potential. The oxidation peak potential and the reduction peak potential of the anode filled with 0mm and 1mm activated carbon particles has small fluctuation with the scanning speed, but the oxidation peak potential of the anode filled with 3mm activated carbon particles increase with the increase of scanning speed and drift toward the positive potential, while the reduction peak potential decreases with the increase of scan rate, moving towards the negative potential. It shows adding 3mm activated carbon particles have impact on electricity generation performance.

Table 1. The oxidation peak potential, reduction peak potential and their radio tested in CV with different anodes and different scanning rates

	Scan Speed/mV•s^{-1}	Anodic peak potentialφpa/v	Reduction peak potentialφpc/v	φθ’=(φpa+φpc)/2 /V	Δφ = （φpa – φpc）/ V	Oxidation current /mA	Reduction current / mA	i_{pa}/i_{pc}
0mm	20	-0.606	-0.422	-0.514	-0.184	3.612751	-3.71535	-0.97238
	50	-0.651	-0.412	-0.5315	-0.239	9.247657	-11.086	-0.83417
	80	-0.646	-0.403	-0.5245	-0.243	14.18974	-20.5	-0.69218
	100	-0.663	-0.398	-0.5305	-0.265	18.7936	-29.3974	-0.63929
	120	-0.637	-0.436	-0.5365	-0.201	18.94198	-32.8177	-0.57719
	150	-0.627	-0.422	-0.5245	-0.205	20.47302	-38.758	-0.52823
1mm	20	-0.487	-0.404	-0.4455	-0.083	6.408862	-7.42556	-0.86308
	50	-0.464	-0.398	-0.431	-0.066	14.78766	-17.3956	-0.85008
	80	-0.481	-0.391	-0.436	-0.09	22.55128	-29.1678	-0.86179
	100	-0.446	-0.413	-0.4295	-0.033	27.15472	-34.9723	-0.77646
	120	-0.428	-0.383	-0.4055	-0.045	30.73666	-37.4483	-0.82078
	150	-0.428	-0.363	-0.3955	-0.065	42.62773	-39.9905	-1.06595
3mm	20	-0.353	-0.541	-0.447	0.188	5.844522	-6.61012	-0.88418
	50	-0.294	-0.582	-0.438	0.288	10.96798	-12.2867	-0.89267
	80	-0.262	-0.601	-0.4315	0.339	14.84695	-17.154	-0.86551
	100	-0.238	-0.608	-0.423	0.37	15.04198	-16.3446	-0.9203
	120	-0.2	-0.61	-0.405	0.41	19.6517	-22.092	-0.88954
	150	-0.179	-0.612	-0.3955	0.433	23.5056	-22.1159	-1.06284

The absolute value of oxidation peak current and reduction peak current increase with the increase of scan speed. The radio of oxidation peak current and reduction peak current of unfilled anode decreases with the increase of scan rate, the radio of oxidation peak current and reduction peak current of anode filled with 1mm and 3mm activated carbon particles stably increase. A linear fit of oxidation peak current and reduction peak current versus scan speed shows unfilled anode peak current is proportional to the 1th power of scan speed, the battery system is the surface control, bacteria transfer electron in the electricity-producing are adsorbed on the electrode. The reduction peak and oxidation peak currents of anode filled 1mm activated carbon particles are proportional to the 0.9th power of scan speed, it shows the battery system is diffusion and surface control, bacteria in the liquid to participate in producing electrical response and the reversibility of the battery system is enhanced, this is consistent with the results of the peak potential judgment. The reduction peak current of anode filled 3mm activated carbon particles is also proportional to the 1th power of scan speed, but the oxidation peak current is also proportional to the 0.7th power of scan speed, in battery system the diffusion control is enhanced, it indicate that in the liquid there are more producing electricity bacteria participate in the oxidation reaction.

All the analysis shows that the oxidation peak current and reduction peak current of anode unfilled activated carbon is proportional to the 1.0th power of scanning speed, but the ratio of the oxidation peak current and reduction peak current decreases gradually with the increase of the scanning speed, anode fluid in the electrode process is irreversible when not filled with activated carbon.

The oxidation peak and reduction peak of anode filled with 1mm granules activated carbon particles appear almost in pairs, the radio of oxidation peak current and reduction peak current is proportional to the 0.9th power of the scan speed and approach to 1 with the increase of scan speed, electrode process of anode filled with 1mm cylindrical activated carbon particle is reversible compared with unfilled activated carbon particle anode. With the anode filled 3mm granules activated carbon particles, oxidation peak current is proportional to the 0.7th power of the scan speed and reduction peak current is proportional to the 1.0th power of the scan speed. Through oxidation peak potential and reduction peak potential respectively positive shift and negative shift, the current radio is proportional to the 2th power of the scan speed; it belongs to partially reversible electrode process.

CONCLUSION

Increase the anode surface area can improve the output power. The power density increases with the increasing of cylindrical activated carbon particle diameter; the performance of anode unfilled was the worst. When cylindrical activated carbon particles diameter is 1mm, the maximum power density is 4056.4mW/m3, apparent internal resistance is 494Ω.

Cyclic voltammetry show the bacterium adsorbed on steel mesh anode filled with activated carbon has activity and with the decreasing of diameter, the surface area increase, the electrochemical activity is enhanced.
In cyclic voltammetry, the oxidation peak potential and the reduction peak potential appear in the negative potential.

Electrode process of anode unfilled is a completely irreversible process, electrode process reversibility of steel mesh anode filled with cylindrical activated carbon is improved, electrode process of steel mesh anode filled with 3mm activated carbon is partially reversible process, electrode process of steel mesh anode filled with 1mm activated carbon approach to reversible process.

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