ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 9, Issue, 01, pp.45658-45664, January, 2017

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

EFFECT OF $K_3FE\ (CN)_6$ ON LONG-TERM ELECTROCHEMICAL POWER OUTPUT OF FOUR SERIES STACK MFCS

[1,*]Bolong Jiang, [1,2]Thorben Muddemann, [1]Ulrich Kunz, [2]Dennis Haupt, [2]Hinnerk Bormann, [2]Michael Niedermeiser, [2]Ottmar Schläfer, [2]Michael Sievers and [3]Sebastian Hofmann

[1]Clausthal University of Technology Institute of Chemical and Electrochemical Process Engineering Leibnizstr.17, D-38678 Clausthal-Zellerfeld, Germany
[2]CUTEC Institut GmbH Leibnizstr.21, D-38678 Clausthal-Zellerfeld, Germany
[3]Clausthal University of Technology Institute of Mechanical Engineering, Robert-Koch Street No.32, D-38678 Clausthal-Zellerfeld, Germany

ARTICLE INFO

Article History:
Received 28th October, 2016
Received in revised form
24th November, 2016
Accepted 14th December, 2016
Published online 31st January, 2017

Key words:

Microbial Fuel Cell
Series Connection
Long-Term Performance
Potassium Ferricyanide.

ABSTRACT

Two single microbial fuel MFCs with different roughness (roughened and without roughened) were firstly constructed and the effect of the roughness on optimal power density was studied. It was found that the power density of MFC with roughened electrodes (50 $mW•m^{-2}$) was two times as high as that of MFC with unroughened electrodes, showing that roughness plays an important role in improving power density. Four series stack MFCs with roughened electrodes were then constructed to further improve power density and long-term performances of the MFCs were studied over 160 days. The effect of $K_3Fe(CN)_6$, which added to catholyte, on power output of the MFCs was also investigated. A maximum power density output of 126.5 $mW•m^{-2}$ was achieved at 62th day with the four series stack MFCs during the long term test. The optimal powers of the MFCs tend to become closer to each other after 160 days, which ranged from 52.0 $mW•m^{-2}$ to 73.4 $mW•m^{-2}$, showing a considerably stable power output was maintained during the period of 160 days. The output power densities of each MFC in the four series stack MFCs increased rapidly with increasing $K_3Fe(CN)_6$ concentration, and a maximum power density output of 560 $mW•m^{-2}$ was observed by injecting 15 mL 200 mM $K_3Fe(CN)_6$ solution into cathode container. This value is 10.8 times of that without adding $K_3Fe(CN)_6$ solution at the same conditions, showing that $K_3Fe(CN)_6$ solution has a significant effect on improving the MFC powers. This study provides a foundation for further development of an industrially relevant MFC for water treatment.

Citation: Bolong Jiang, Thorben Muddemann, Ulrich Kunz, Dennis Haupt, Hinnerk Bormann, Michael Niedermeiser, Ottmar Schläfer, Michael Sievers and Sebastian Hofmann, 2017. "Effect of $K_3Fe\ (CN)_6$ on long-term electrochemical power output of four series stack MFCs", *International Journal of Current Research*, 9, (01), 45658-45664.

INTRODUCTION

Driven by the increasingly serious energy shortages and the growing awareness of environmental protection, looking for new alternative energy has attracted a great deal of attention.
A MFC is a newly developed device that uses energy from waste waters by bio-electrochemical reactions (Li *et al*., 2017). Power output by MFCs has increased considerably over the last decade due to several scientific and technical advances (Prashant *et al*., 2016). In an MFC, microorganisms in the anode chamber degrade (oxidize) organic matter, producing electrons that travel through a series of respiratory enzymes in the cell and make energy for the cell in the form of adenosine triphosphate (ATP).

****Corresponding author: Bolong Jiang,***
Clausthal University of Technology Institute of Chemical and Electrochemical Process Engineering, Leibnizstr.17, D-38678 Clausthal-Zellerfeld, Germany.

The electrons are then released to a terminal electron acceptor (TEA) which accepts the electrons and becomes reduced. For example, oxygen can be reduced to water through a catalyzed reaction of the electrons with protons. The electricity produced biochemically is sustained yet environmentally friendly (Lin *et al*., 2015). Comparing to the current technologies used for generating energy from organic matter, the MFC technology has important advantages: i) MFCs allow the direct conversion of substrate energy to electricity with high conversion efficiency. ii) MFCs operate efficiently at ambient conditions, and even at low temperatures, which distinguishes this technology from all current bio-energy processes.iii) MFCs do not require gas treatment because the off-gasses of these devices are enriched in carbon dioxide and normally have no useful energy content (Hernández-Fernández *et al*., 2015). MFC hold promise as a green technology for bioenergy production (Bruce, 2008). However, MFC is still in its infant

and the majority of work has been focused on its technical feasibility and fundamental characteristics. The greatest limitation of this technology is the low power density output and subsequent scaling-up (Hernández-Fernández *et al*., 2015). The power density output in MFCs have increased 5–6 orders of magnitude over the last decade as a result of the optimization of reactor configuration, the improvement of operational parameters, the selection of bacteria with greater electrochemical activity, and the application of novel electrode materials (Wang *et al*., 2014). In order to improve the performance of MFCs, many works have focused on electrode modification, such as ammonia treatment (Cheng, 2007), electrochemical treatment (Liang *et al*., 2017; Zhou *et al*., 2012), metal oxide doping (Hou *et al*., 2016; Ravinder *et al*., 2016), and polymer odification (Lai *et al*., 2011), etc. Anodic microbes degrade organic matters and release electrons to the surface of anode, therefore, the power output of MFC depends strongly on the electrode surface properties (Mirella *et al*., 2010). In general, the output power of MFC increases with using higher surface area materials (Chaudhuri, 2003). Aelterman *et al*. (2008) proved the benefits of a three dimensional anode, by analyzing the electrochemical performance of two-chambered MFCs characterized by five different anodes. It was found that packing materials in the anode chamber can extend the superficial anode area and increase microbial enrichment on the anode surface, which leads to improvement of power density output of MFCs. Results showed that GAC-packed MFC showed the most stable voltage output (higher than 200 mV for 576 h) and lowest mass transfer resistance than GG-packed and non-packed MFCs owing to the stronger adsorption ability (Guo *et al*., 2016). Improving the surface roughness, which is beneficial for microorganisms settlement and reaction between microbial and reactants, is an easy way to increase the surface area of electrodes. A three-electrode system was used to study the effect of anode surface roughness on the performance of microbial fuel cells (MFCs) (Zhou *et al*., 2012). They found that the current density generated by the rough electrode was much higher than that generated by the smooth one.

Studies on optimize MFC configurations were carried out to improve power density output of MFCs (Oliveira *et al*., 2013). MFC units connected in series or in parallel are a promising strategy to achieve enhanced output of voltage and current for practical application of MFC technology (Zhuang *et al*., 2012; Oh, 2007; Ieropoulos, 2010; Ieropoulos *et al*., 2008). Several literatures have also tested the stacked MFCs to improve electric power that can be used for electrical devices (e.g., pumps, sensors) (An *et al*., 2016; Donovan *et al*., 2008; Ledezma *et al*., 2013). Dong *et al*. (2013) designed a single chamber membrane-less microbial fuel cell which simulated the colonic environment. It was used to provide bioenergy for implantable medical devices. However, the power generated by this novel continuous MFC (1.6 mW) was not sufficient to power devices with high energy requirement. Aelterman *et al*. (2013) obtained enhanced voltages (up to 2.02 V) and currents (up to 255 mA) by connecting six MFC stacks in series and in parallel, respectively. As mentioned above, one of the greatest limitations of this technology is the subsequent scaling-up. The scale of MFC system must be increased to meet the requirements for large-scale wastewater treatment and bio electricity production. To increase the dimension of an individual MFC unit is one approach for scale-up. However, connecting a large number of small-size units together rather than increasing the size of an individual unit would be more successful (Ieropoulos *et al*., 2008). A 10-liter serpentine-type microbial fuel cell (MFC) stack was constructed by extending 40 tubular air cathode MFC units in a 3-D alignment pattern, which could produce an open circuit voltage of 23.0 V and a maximum power density of 4.1 W/m3 (at 0.7 A/m3) (Zhuang *et al*., 2012). In this study, the surfaces of electrodes were collided with sand particles. By this way, we obtained electrodes, whose surfaces were roughened. Two single microbial fuel MFCs with different roughness (roughened and without roughened) were firstly constructed and the effect of the roughness on optimal power density of the single MFC was studied. It was found that the MFC with roughened electrodes showed much higher optimal power density than that without roughened. Four series stack MFCs with roughened surface electrodes were constructed to further improve power density and long-term performances of the MFCs were studied over 160 days. The coulombic and energy efficiencies were calculated. Since power production from MFCs can be limited by the overpotential of the oxygen reduction reaction (ORR) at the cathode (Ahn *et al*., 2014), measures are taken to improve the performance of cathode, one of which is to add Potassium ferricyanide ($K_3Fe(CN)_6$) to catholyte. The effect of $K_3Fe(CN)_6$ concentration in catholyte on the power output of the four series stack MFCs was also studied. The results from these comparisons may lay the foundation for further development of an industrially relevant MFC for water treatment.

MATERIALS AND METHODS

Measurement of Roughness

The roughness of electrode plates is measured in Institute of Mechanical Engineering (University Clausthal of Technology, Germany),who uses the MarSurf GD 120 (Mahr Corporation, Germany) to measure the roughness. During the measurement, a test probe is contacted on the surface of electrode plate and the facility scans for a certain distance (for electrode plate without sand collision 12.5 mm and for electrode plate with sand collision 40.2 mm) with different scanning scales (for electrode plate without sand collision 2.5 mm and for electrode plate with sand collision 8 mm) to measure the arithmetic mean roughness and the average rough deepness of the two different electrode plates.

Wastewater and COD substrate

The main components of model wastewater used for the reaction of MFC: $NaAc{\cdot}3H_2O$ = 0.21 $g{\cdot}L^{-1}$, glucose = 0.05 $g{\cdot}L^{-1}$, ribose = 0.05 $g{\cdot}L^{-1}$, glycine = 0.16 $g{\cdot}L^{-1}$, (L-)Cystein = 0.15 $g{\cdot}L^{-1}$, potassium hydrogen phalate = 0.09 $g{\cdot}L^{-1}$, NH_4Cl = 0.31 $g{\cdot}L^{-1}$, KCl = 0.13 $g{\cdot}L^{-1}$, $NaHCO_3$ = 0.10 – 0.15 $g{\cdot}L^{-1}$, vitamine with heavy metal = 12.5 $mL{\cdot}L^{-1}$. All the components except Na_2CO_3 are mixed with deionized water. The mixture is than stirred by magnetic mixer. Na_2CO_3 is added to the mixture continuously in order to set the pH value to the range of 8.6 – 8.8. The main components of COD substrate: $NaAc{\cdot}3H_2O$ = 44.32 $g{\cdot}L^{-1}$, glucose = 10.32 $g{\cdot}L^{-1}$, ribose = 9.38 $g{\cdot}L^{-1}$, glycine = 31.2 $g{\cdot}L^{-1}$, (L-) Cystein = 30.3 $g{\cdot}L^{-1}$.The COD substrate is used not only for the nutrient of microorganism, but also for additional reactant of anode in our experiments.

Design of MFC

The each MFC reactors in the stack used in this study were constructed of stainless steel, with anodic and cathodic plates

separated by a Nafion 117 membrane. Both anode and cathode were prepared by polymer carbon composite (approximately 85% graphite in an olefinic polymer binder from Eisenhuth Corporation, Germany,) with channels acrossed on surface of the electrode (Fig. 1). The surfaces of which were collided with sand particles to increase their surface roughness (which denoted as roughened electrode). Each electrode has a dimension of 25 × 14 × 1 cm. The four individual MFCs with roughened electrodes were connected in series (Fig. 2) and denoted as MFC#1, MFC#2, MFC#3 and MFC#4, respectively. As can be seen from Fig. 2, the whole stack is connected with two glass containers of 2 L for anodic and cathodic reactants. The nutrition and wastewater are only put into the container at the anode of MFC#1, while the bubbling air flows into the container at cathode of MFC#4. The cathode water was enriched with air by bubbling air through the catholyte reservoir. Oxygen in the anode chamber would inhibit electricity generation. Therefore, the system must be designed to keep the bacteria separated from oxygen, which can be realized by using a membrane or separator. Moreover, the separator should also be used for proton exchange. Nafion 117, which mainly made of sulfonated tetrafluorethylen-polymer (PTFE), is used as proton exchange membrane between the anode and cathode. Nafion has several advantages in traditional H_2/O_2 fuel cells, such as its high stability against degradation. The waste water (using NaAc as additional nutrition for the microorganism) was feed through the cathode and the anode compartment by two pumps.

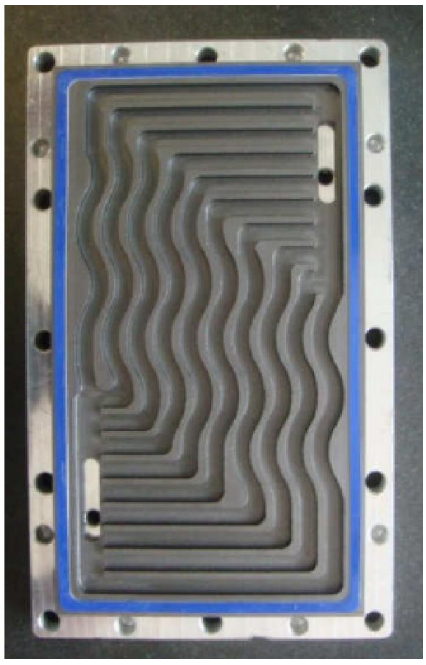

Fig.1. Picture of electrode

Measurement of COD values

A standard method is used to determine the chemical oxygen demand (COD). During the measurement, 2 mL of sample from the anode water were taken to determine the COD by using a commercial COD analyzer, which is produced by Macherey-Nagel Corporation (Germany), type: Nanocolor UV/VIS. The COD values are measured under standard condition (298 K and 1 atm). Generating power is one of the main goals of MFC operation, therefore it is necessary to convert as much as possible of the biomass into current and to recover as much energy as possible from the system.

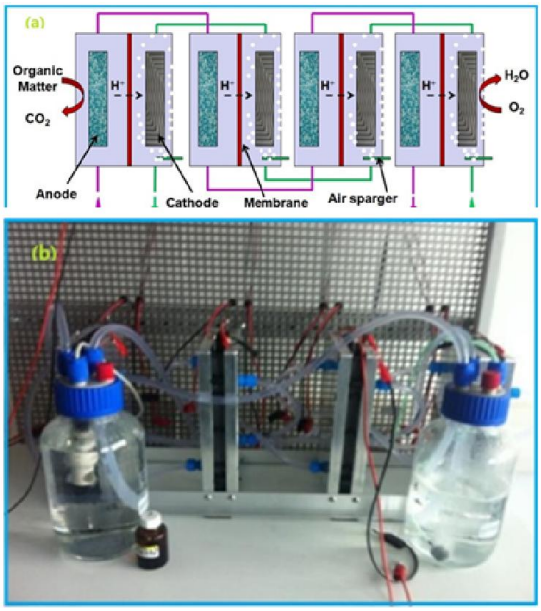

Fig. 2. Four individual MFCs connected in series (a) scheme of the MFC stack (b) photograph of the MFC stack

Coulombic and energy efficiency

Coulombic efficiency

One of the most important parameters to evaluate the efficiency of MFC is coulombic efficiency, which is defined as follows,

$$\eta = \frac{\text{Coulombs recovered}}{\text{Total coulombs in substrate}} \quad (1)$$

Where η is the coulombic efficiency. According to Eq.(1), the coulombic efficiency η can be calculated by the following equation,

$$\eta = \frac{M \int_0^t I \, dt}{FbV_{An}\Delta COD} \quad (2)$$

Energy efficiency

The energy efficiency is based on energy recovered in the system compared to the energy content of the starting material. Therefore, it is defined as the following equation,

$$\eta_E = \frac{E}{E_{max}}\eta \quad (3)$$

With η_E as the energy efficiency; E as cell-voltage; E_{max} as the maximum voltage of MFC. In our experiments we set a current of 2.5 mA for the determination of this parameter, while the voltage of the MFC is 180 mV. The maximum potential of MFC can be calculated by the following equation,

$$E_{max} = \frac{-\Delta G}{bF} \quad (4)$$

With ΔG (gibbs' enthalpy).

RESULTS AND DISCUSSION

Roughness for different electrode plates

Table 1 shows the arithmetic mean roughness (R_a) and the average rough deepness (R_z) of the two different electrode

plates (roughened and without roughened). It can be seen that the R_a of electrode plate with sand collision is 11.8 μm, which is more than two times of that of electrode plate without sand collision (4.9 μm). The similar phenomenon is also observed for the R_z.

Table 1. Comparison of roughness between different electrode plate

Electrode plates	R_a/μm	R_z/μm
Electrode plate without roughened	4.9	39.34
Electrode plate roughened	11.8	74.2

Performance of single MFCs

The polarization curves of the single MFCs with electrodes of different roughness are shown in Fig. 3. The data suggested that the optimal power density of the single MFC with roughened electrodes has reached 50 $mW \cdot m^{-2}$, while the optimal power density of MFC with unroughened was only 20 $mW \cdot m^{-2}$, showing that roughness plays an important role in improving the power density of MFC. The main reason is that higher roughness is beneficial to development of microorganisms. According to Fig. 3 (b), the optimal power densities of MFCs with and without roughened electrode are reached 2 mA and 6 mA, respectively.

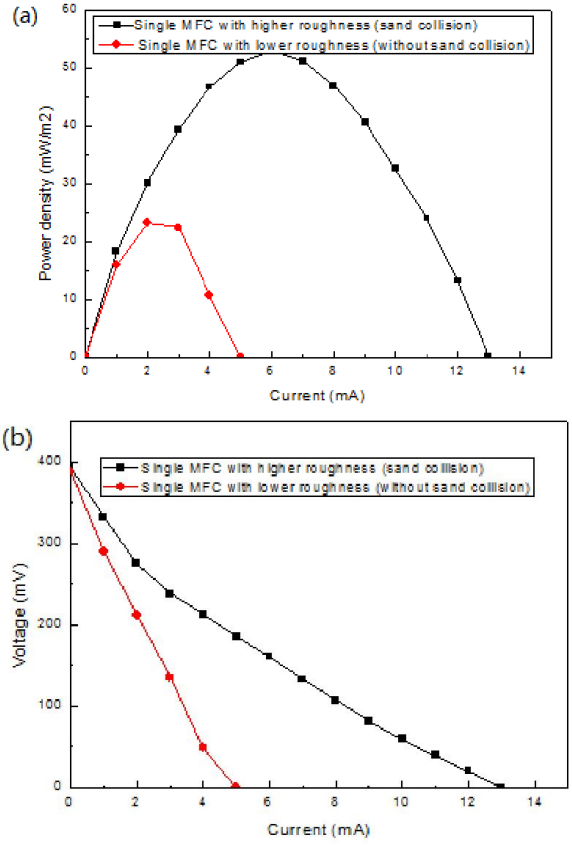

Fig. 3. Polarization curves of the single MFCs with electrodes of different roughness (roughened and without roughened)

Performance of roughed MFCs in series and its long term performance

The four single MFCs with roughened electrode were connected in series to further improve power density. The polarization curves of the four series stack MFCs with are shown in Fig. 4. The data suggested that MFC#1 and MFC#4 produce relatively higher power densities than MFC#2 and MFC#3.Theoretically, the optimal powers of these fuel cells should be equally high. The main reason for the different values of optimal power is probably because of the different development of microorganisms in the four cells, since metabolic activities play an important role. Another reason is that the reactants in wastewater and nutrition (NaAc) are not uniformly distributed. As it is shown in Fig. 2, two containers are put into use to support the chemical reactions inside the MFCs. However, the nutrition and wastewater are only put into the container at the anode of MFC#1, while the bubbling air flows into the container at cathode of MFC#4, results in to the result that is mentioned above. Fig. 4 also aggregates a series of voltage curves against current. The data suggested that the voltage descends with increase of current and it becomes zero at the end of the measurement because of the resistance of mass transport. It can be observed that the MFCs with higher power densities (MFC#1 and MFC#4) possess also a relatively higher voltage.

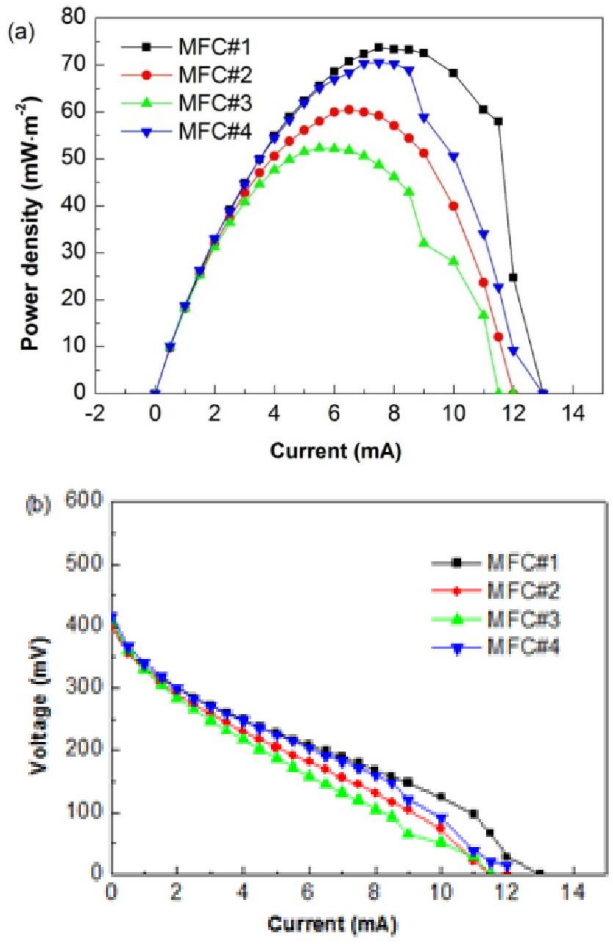

Fig. 4. Polarization curves of the four series stack MFC with roughened electrodes

Fig. 5 illustrates the long-term performance of the four series stack MFCs, which were continuously operated for 160 days. Within 12 days, the optimal power of each MFC increased with time. Then, the power densities fluctuated around a value. And the optimal power density of each MFC became different from each other gradually after 3 days. Despite of the different optimal power density, the similar tendency is observed for each MFC in the four series stack MFCs. Significant decrease in optimal power of MFCs is observed at the 42th and 102th days which is apparent that there not enough wastewater and nutrient to support the operation of microorganisms and MFCs.

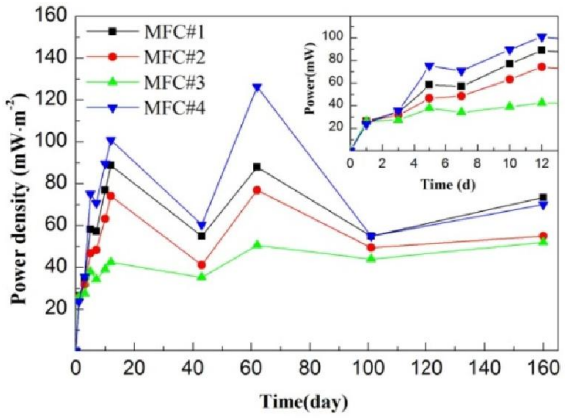

Fig. 5. The long-term performance of the four series stack MFCs with roughened electrodes

The optimal power decreased in the sequence: MFC#4> MFC#1>MFC#2>MFC#3. The best performance was achieved at 62 days. The optimal powers of each MFC at 62th and 160th day are shown in Table 2, which suggests that the optimal power of MFC#4 reached 126.5 mW·m^{-2} at 62th day. Zhuang *et al.*[28] reported a maximum power density of 65.4 mW·m^{-2} and 97.2 mW·m^{-2} produced from forty series stack MFC sand forty series-parallel stack MFCs fed with brewery wastewater (between days 25 and 35), respectively. Our results showed that the electrical performance of the four series stack in the current study is comparable to the best stack documented thus far. At the end of the experiment (160th day), the MFC#4 in the four series stack produced a maximum power density of 70.05 mW·m^{-2}, a decrease of 44.6% from the highest density obtained at 62th day (126.5 mW·m^{-2}). However, for MFC#1 and MFC#2, the decrease from the highest power density obtained at day 62th to the end of the experiment (160th day) were 16.6% and 21.7%, respectively. For MFC#3 produced the lowest power density among these four MFCs, the power density keeps more stable during the whole experiment. Zhuang *et al*. (2012) evaluated the long-term performance of their forty series stack MFCs. At the end of the experiment, their stack produced a maximum power density of 25.5 mW·m^{-2}, a decrease of 60% from the highest density obtained at day 30 (65.4 mW·m^{-2}). In summary, the optimal powers of the four MFCs tend to become closer to each other after 160 days, which ranged from 52.0 mW·m^{-2} to 73.4mW·m^{-2}, showing a considerably stable power output during the period of 160 days.

Table 2. Optimal powers of the four MFCs with roughened electrodes at 160th day

MFC	Maximum Power (mW)		Maximum Power Density (mW·m^{-2})	
	62th day	160th day	62th day	160th day
MFC#1	1.60	1.34	88.0	73.4
MFC#2	1.40	1.10	77.0	60.4
MFC#3	0.92	0.95	50.6	52.0
MFC#4	2.30	1.28	126.5	70.1

Discussion of Coulombic and energy efficiency

NaAc are used as substrate for the MFCs in the experiment. Therefore, the chemical reaction is shown as follows,

$$CH_3COO^- + O_2 \longrightarrow HCO_3^- + H^+$$

The maximum potential of the whole system is 1.09 V. (Annemiek *et al*., 2006) The average potentials of the each MFC in the four series stack MFCs, which were obtained directly from LabVIEW system, are shown in Table 3, from which the average potential of the four MFCs is determined as 223.2 mV.

Table 3 Potentials of four series stack MFCs

MFCs	Potential (mV)	Average potential (mV)	Energy efficiency (%)
MFC#1	238.2	223.2	5.47
MFC#2	217.3		
MFC#3	201.5		
MFC#4	235.8		

The COD removal is needed for coulombic energy calculations. In order to calculate the COD difference (ΔCOD), both the start and end samples were detected. The results of change in COD (ΔCOD) values for the four series stack MFCs are shown in Table 4.

Table 4. COD values of the start and end samples for the four series stack MFCs with roughened electrodes

Day	COD (mg·L^{-1})		Duration (h)	Current (mA)
	Start sample	End sample		
159th	2888	2836	19.2	4.5
160th	3665	3565	18.8	5.5

The COD value measurement at 159th day (Table 3) is taken as an example for energy efficiency calculation. The measurement interval and ΔCOD are 19.2 h and 52 mg·L−1, respectively. According to Eq.(2), the coulombic efficiency of the four MFCs is calculated as 26.8%, which corresponds the theoretical value in the range of 12 – 95% (Bruce, 2008). Aelterman *et al.* (Aelterman *et al*., 2006) have obtained coulombic efficiency of 12.4% by connecting six MFC stacks in series, which is lower than 26.8%. Appling the Eq.(3)–(4), the energy efficiency is calculated to be 5.47%. Logan *et al* [5] have obtained a value range of coulombic efficiency, which lies in the range of 2 – 50%, which means that the result corresponds to the theoretical value.

Performance of MFCs with $K_3Fe(CN)_6$ as catholyte

Since power production from MFCs can be limited by the overpotential of the oxygen reduction reaction (ORR) at the cathode (Ahn *et al*., 2014), measures are taken to improve the performance of cathode. One of the methods is to add cathodic fuel to the catholyte. In this experiments, $K_3Fe(CN)_6$ solutions with different concentrations (50 mM, 100 mM and 200 mM) were prepared. And the pH values of which are set to 7 by sodium carbonate. During the experiments, the $K_3Fe(CN)_6$ solution was injected into the cathode container. The obtained results are shown in Fig. 6. It can be seen from Fig. 6 that the output power density of the MFCs without adding $K_3Fe(CN)_6$ solution were around 52 − 73 mW·m^{-2}. With increasing $K_3Fe(CN)_6$ concentration to 100 mM, the output power densities increased slowly at initially, then increased rapidly. However, with further increasing $K_3Fe(CN)_6$ concentration from 100 mM to 200 mM the increase became slow. Choi *et al.* (2006) have measured cyclic voltammograms of thionin and $Fe(CN)_6^{3-}$ in pH = 7 phosphate buffer at a carbon electrode. Results show that reduction of Fe $(CN)_6^{3-}$ is diffusion controlled. Fe $(CN)_6^{3-}$ could easily reduced to $Fe(CN)_6^{4-}$, indicates that this species is an ideal cathodic fuel. Bruce *et al*. (2004) also reported that the internal resistance

with the 22.5 cm^2 Pt cathode and dissolved oxygen was 960 Ω, while the internal resistance of the system with ferricyanide was only 800 Ω.

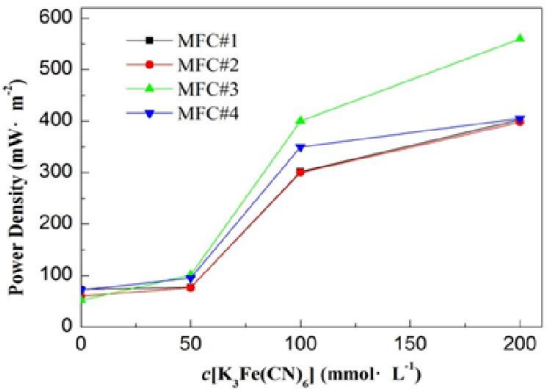

Fig. 6. Improvement of MFCs powers by adding $K_3Fe(CN)_6$ to catholyte

Thus, the improved power densities can be explained by the great mass transfer efficiency with concentrated ferricyanide. At low lower $Fe(CN)_6^{3-}$ concentration, the reduction is mass transfer controlled. As a result, the output power density increased slowly with increasing $K_3Fe(CN)_6$ solution owing to the lower reduction speed of $Fe(CN)_6^{3-}$. At higher concentration of $K_3Fe(CN)_6$, the effect of $Fe(CN)_6^{3-}$ on the output power densities is significant since large amount of $Fe(CN)_6^{3-}$ can be reduced to $Fe(CN)_6^{4-}$ rapidly. Among the four series stacked MFCs, the output power density of MFC #3 is the highest, which reaches 560 $mW \cdot m^{-2}$ at $K_3Fe(CN)_6$ concentration of 200 mM. This value is 10.8 times of that MFC#3 without adding $K_3Fe(CN)_6$ solution at the same conditions. Aelterman *et al.* (2006) have prepared $K_3Fe(CN)_6$ catholyte with KH_2PO_4 as buffer solution and obtained the similar results. The output power densities have almost tripled with the value of 308 $W \cdot m^{-3}$ (series) and 263 $W \cdot m^{-3}$ (parallel).

Conclusion

The higher surface roughness electrodes, which achieved by colliding the surface of the electrodes by sand particles, were constructed. Two single microbial fuel MFCs with different roughness (roughened and without roughened) were firstly constructed and the effect of the roughness on optimal power density of the single MFC was studied. The power density of single MFC with roughened electrodes is 50 $mW \cdot m^{-2}$, which is two times as high as that of MFC with electrodes without treated by sand collision, showing that roughness plays an important role in improving power density. The four series stack MFCs were constructed with the roughened electrodes to further improve the power density and the long-term performances of the MFCs were studied over 160 days. Results showed that the optimal power of the four series stack MFCs decreased in the sequence: MFC#4> MFC#1>MFC#2> MFC#3. A maximum power density output of 126.5 $mW \cdot m^{-2}$ was achieved at 62th day, which shows that series connection of MFCs can improve the power output. The optimal powers of the four MFCs were kept stable after 62th day and tend to become closer (which ranged between 52.03 and 73.41m $W \cdot m^{-2}$) to each other at 160th day. The coulombic efficiency of the four series stack MFCs is 26.8%, while the energy efficiency is 5.47%. The output power densities of each MFC in the four series stack MFCs ascend rapidly with increasing $K_3Fe(CN)_6$ concentration, a maximum power density output of 560 $mW \cdot m^{-2}$ was observed at $K_3Fe(CN)_6$ concentration of 200 mM. This value is 10.8 times that of without adding $K_3Fe(CN)_6$ solution at same conditions. Our results showed that the electrical performance of the four series stack in the current study is comparable to the best stack documented thus far.

Acknowledgement

The authors would like to thank Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung), BMBF, Germany, for funding parts of this study under the contract No. WTER0219813.

REFERENCES

Aelterman, P., K. Rabaey, H. T. Pham 2006. Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. *Environ Sci Technol.,* 40(10), 3388-3394.

Aelterman, P., M. Versichele, and M. Marzorati 2008. Loading rate and external resistance control the electricity generation of microbial fuel cells with different three-dimensional anodes.*Bioresour.Technol*., 99, 8895-8902.

Ahn, Y., I. Ivanov., and C. Tharamani. 2014. Mesoporous nitrogen-rich carbon materials as cathode catalysts in microbial fuel cells. *J.Power Sources*, 269, 406-412.

An, J., J. Sim, and Y. J. Feng 2016. Understanding energy loss in parallelly connected microbial fuel cells: Non-Faradaic current. *Environ. Bioresour.Technol.,* 203, 280-286.

Annemiek, T., H. V. M. C. Hamelers and C. Buisman 2006. A bipolar membrane combined with ferric iron reduction as an efficient cathode system in microbial fuel cells. *Environ. Sci. Technol.,* 40, 5200-5250.

Bruce, L. 2008. Microbial Fuel Cells (M). *A John Wiley& Sons, Inc., Publication*, 1-216.

Chaudhuri, S. K., D. R. Lovley 2003. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. *Nat. Biotechnol*., 21, 1229-1232.

Cheng, S., L. Bruce 2007. Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells. *Electrochem. Commun*., 9, 492.

Dong, K., B. Jia, and C. Yu 2013. Power Approaches for Implantable Medical Devices. *Biosens.Bioelectron.,* 41, 916-919.

Donovan, C., A. Dewan, and D. Heo 2008. Batteryless, Wireless Sensor Powered by a Sediment Microbial Fuel Cell. *Environ.Sci.Technol.,* 42, 8591-8596.

Guo, X., Y. L. Zhan, C. M. Chen, and B. Cai 2016. Influence of packing material characteristics on the performance of microbial fuel cells using petroleum refinery wastewater as fuel. *Renewable Energy*, 87, 437-444.

Hernández-Fernández, F.J., A. Pérez de los Ríos, and M. J. Salar-García 2015. Recent progress and perspectives in microbial fuel cells for bioenergy generation and wastewater treatment. *Fuel Process. Technol.,* 138, 284-297.

Hou, Y., H. Yuan, Z. Wen, and S. Cui 2016. Nitrogen-doped graphene/CoNi alloy encased within bamboo-like carbon nanotube hybrids as cathode catalysts in microbial fuel cells. *J. Power Sources*, 307, 561-568.

Ieropoulos, I., J. Greenman 2010. Improved energy output levels from small-scale Microbial Fuel Cells. *Bioelectrochem.,* 78,44-50.

Ieropoulos, I., J. Greenman, and C. Melhuish 2008. Microbial fuel cells based on carbon veil electrodes: Stack configuration and scalability. *Int. J.Energy. Res*., 32, 1228-1240.

Lai, B., X. Tang, and H. Li 2011. Power production enhancement with a polyaniline modified anode in microbial fuel cells. *Bioelectron*., 28, 373.

Ledezma, P., A. Stinchcombe, and J. Grennman 2013. The first self-sustainable microbial fuel cell stack.*Phys. Chem. Chem. Phys.,* 15, 2278-2281.

Li, Y. H., L. F. Liu, and F. L. Yang 2017. Destruction of tetracycline hydrochloride antibiotics by FeOOH/TiO_2 granular activated carbon as expanded cathode in low-cost MBR/MFC coupled system. *J.Membr. Sci.,* 525, 202–209.

Liang, Y. X., H. J Feng, D. S. Shen, N. Li, K. Guo, Y. Y. Zhou, J. Xu, and W. Chen 2017. Enhancement of anodic biofilm formation and current output in microbial fuel cells by composite modification of stainless steel electrodes. *J.Power Sources,* 342, 98-104.

Lin, C. W., C. H. Wu, and W. T. Huang 2015. Evaluation of different cell-immobilization strategies for simultaneous distillery wastewater treatment and electricity generation in microbial fuel cells. *Fuel*., 144, 1-8.

Mirella, D. L., S. Keith, and P. C. Tom 2010. Effect of increasing anode surface area on the performance of a single chamber microbial fuel cell. *J. Chem. Eng.,* 156, 40-48.

Oh, S. E., M. Booki, and B. Logan. 2004. Cathode Performance as a Factor in Electricity Generation in Microbial Fuel Cells*. Environ. Sci. Technol.,* 38, 4900-4904.

Oh, S., B. Logan 2007. Voltage reversal during microbial fuel cell stack operation. *J.Power Sources*. 167, 11-17.

Oliveira, V. B., M. Simões, and L. F. Melo 2013. Overview on the developments of microbial fuel cells. *Eng. J.,* 73, 53-64.

Prashant P., N. Vikas, L. Shinde Rajendra, P. Deopurkar Sharad, A. KaleSunil, and D. Patil 2016. Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery. *Appl. Energy*, 168, 706–72.

Ravinder, K., S. Lakhveer, and A.W. Zularisam, 2016. Potential of porous Co_3O_4 nanorods as cathode catalyst for oxygen reduction reaction in microbial fuel cells. *Bioresour. Technol.,* 220, 537-542.

Shin, S. H., Y. Choi, S. Na 2006. Development of Bipolar Plate Stack Type Microbial Fuel Cells. *Bull.Korean Chem.Soc*., 27, 281-285.

Wang, Z. J., Y. C. Wu, and L. Wang 2014. Polarization behavior of microbial fuel cells under stack operation. *Chin. Sci. Bull.,* 59, 2214-2220.

Zhou, M., M. Chi, and H. Wang 2012. Anode modification by electrochemical oxidation: A new practical method to improve the performance of microbial fuel cells. *Biochem. Eng. J*., 60, 151.

Zhou, Y., H. Junbo, and W. Michael 2012. Effect of Anode Surface Roughness on Power Generation in Microbial Fuel Cells. *ASEM 2012 International Mechanical Engineering Congress and Exposition.* 6, 1409-1414.

Zhuang, L., Y. Yuan, Y. Q. Wang 2012. Long-term evaluation of a 10-liter serpentine-type microbial fuel cell stack treating brewery wastewater. *Bioresour.Technol*., 123, 406-412.

Zhuang, L., Y. Zheng, and S. Zhou 2012. Scalable microbial fuel cell (MFC) stack for continuous real wastewater treatment.*Bioresour.Technol.*106, 82-88.

****