



Evaluation of Microbial Fuel Cells with Graphite Plus MnO₂ and MoS₂ Paints as Oxygen Reduction Cathode Catalyst

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For the improvement of microbial fuel cell (MFC) performance in real wastewater it is necessary to implement catalysts on the cathode. Potential electrochemical catalysts for the MFC have to be widely available and should be low cost materials. Graphite, MnO₂ and MoS₂ fulfill the requirements and were evaluated in this work. These materials were prepared by dispersion of MnO₂ and/or MoS₂ and graphite in a solution of celluloid using butanone as solvent. Four MFCs with an active area of 225 cm² were connected in series with the wastewater supply. Their individual maximum output power densities were evaluated in relation to time. The results showed that MFC without catalyst reached a power density of only 40 mW/m², while the best performance of MFC with graphite plus MnO₂ coating (10:1) was higher than 100 mW/m². Comparing with graphite plus MnO₂ coating, the graphite plus MoS₂ paint shows a lower power density but much higher long-term stability than graphite plus MnO₂ coating. The scaling up of MFC with catalyst on the cathode is also studied in this research. Four MFCs with dimension of 980 cm² were constructed and connected in series, whose anodes have two sides for enlargement of reaction surface area.

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Rising demand for energy and fossil fuel resources being finite, the search for new alternative sustainable energy solutions have increased tremendously.¹ Hydraulic, wind and solar radiation are clean energy resources as alternatives to fossil resources to produce electricity. However, these energy sources are limited by climate and geographical factors. Comparing with the energy sources that are mentioned above, biomass is one of the important renewable carbon sources and has been recognized as a promising energy supplier in the future. The increasing demand for biofuels has encouraged researchers and politicians worldwide to find sustainable biofuel production systems in accordance with the regional conditions and needs.²

A MFC is an innovative method to generate electricity from organic matter using exoelectrogenic bacteria.³ Furthermore MFCs have drawn increasing attention as they can generate renewable energy and purify wastewater simultaneously.⁴ The main MFC-components are the electrodes, separated into the anodic- and cathodic-chamber. Electrons and protons are produced on the anode from the oxidation of organic matters using bacteria as biocatalyst. In the cathode chamber, an electron acceptor is reduced with the electrons transferred via an external circuit and the protons diffused through the solution.⁵ However, complete treatment of wastewater cannot be accomplished solely with MFCs as current production is rapidly reduced to low levels when the chemical oxygen demand of the organic matter is reduced to ~100–200 mg/L.^{6,7} Scaling up MFCs is challenging based on the need to use inexpensive and non-precious metal materials and to achieve good performance. The use of carbon fiber brushes provides a route to make low-cost anodes,^{8–10} and several different cathodes have been constructed without precious metals using activated carbon (AC) as a catalyst.^{11,12} Deepak Pant et al.¹³ have developed non-platinized activated charcoal and graphite electrodes and used as oxygen reducing cathodes instead of the conventional platinized electrodes. They found that these electrodes showed a better performance in the presence of acetate under MFC conditions with pH value of seven and room temperature for oxygen reduction. Current densities of -0.43 mA/cm^{-2} for a non-platinized graphite electrode and -0.6 mA/cm^{-2} for a non-platinized activated charcoal electrode at -200 mV vs. Ag/AgCl reference electrode were obtained. Yolanda

et al.¹⁴ reported a multilayered electrode, which consists of a current collector (metalgauze), an active layer (electro-catalyst on a carbon support embedded in a porous polymer matrix) and a hydrophobic gas diffusion outer layer, which is developed for cogeneration of chemicals and electricity. They found that non-platinized electrodes can offer an acceptable performance for NO reduction. In the single cell set-up, current densities of -12 mA/cm^{-2} for a non-platinized electrode and -10 mA/cm^{-2} for a non-catalyzed activated charcoal electrode were obtained at 50 mV cell voltage, which shows carbon is a good catalytic material. In order to improve the performance of MFCs, many works have focused on electrode modification, such as electrochemical treatment,¹⁵ metal oxide doping¹⁶ and polymer modification.¹⁷

Performances of MFCs using various oxidants in the catholyte have been reported in literature.¹⁸ However, the oxygen from air is the most promising oxidant for MFC application because of free and abundant availability, and high redox potential.¹⁹ Studies show that oxygen reduction and electron acceptance in the cathode chamber have been found as limiting factors for electricity production, due to the slow reaction kinetics of the oxygen reduction reaction.²⁰ The ideal oxygen reduction reaction (ORR) catalysts used in MFCs should be cost-effective and possess high catalytic activity and durability.²¹ In addition the chosen materials should not give off substances which endanger the quality of our water. Conventional platinum (Pt) and gold (Au) based catalysts have always been the best ORR catalysts as they exhibited a reduction of oxygen via a four-electron reduction pathway.^{22,23} However, the high cost of platinum (Pt) catalysts and other precious metals used for ORR further rendered them as not suited for practical applications.²⁴ Furthermore, owing to its sensitivity to poisoning, the performance of a Pt based cathode may be substantially diminished in the presence of a variety of chemicals found in wastewater.²⁵ Recently, a variety of non-precious metal catalysts have been used for MFC applications.²⁶ ORR catalysts are generally used for oxygen cathodes to reduce the overpotential and obtain more energy, which are usually based on metals, carbon, conductive polymers and microbes.²⁷ Carol Santoro et al.²⁸ have developed new iron-based platinum group metal-free catalysts based on low cost organic precursors named niclosamide and ricobendazole for the ORR. The catalysts demonstrated unprecedented performance yielding a power density 25% higher than that of Pt and roughly 100% higher than AC used as a control. Manganese dioxide is considered as a

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promising cathode catalyst for alkaline fuel cells and metal-air batteries,²⁹ since oxygen reduction activities can be achieved on manganese dioxide in alkaline media.^{30,31} Moreover, because of the low cost, being nontoxic and environmentally friendly, having high chemical stability and catalytic activity, manganese dioxide was also considered to be one of the most effective materials for MFC catalysts.^{32,33} Xiang Li et al.^{34,35} have studied manganese oxides with a cryptomelane-type octahedral molecular sieve (OMS-2) structure to replace platinum as a cathode catalyst in MFCs. The power densities of MnO₂ catalysts, which are doped with copper and cobalt, have reached a value of 180 mW/m². Through the 600 hours continuous flow tests, they have found that MnO₂ catalysts doped with copper (Cu-OMS-2) and cobalt (Co-OMS-2) achieved the stable voltage generation of 200 ± 8 mV and 190 ± 5 mV, respectively, which were 50–60 mV higher than that of Pt in MFCs. It is therefore not surprising to find extensive studies on MnO₂ in MFCs. However, most of the MnO₂ achieved maximum power densities (MPD) are only half of Pt based cathodes, regardless of structure modifications or doping with other transition metals.^{34,36,37} Furthermore, the properties and activity of MnO₂ can be highly affected and reduced upon agglomeration to a bulk material, resulting in unsatisfactory electrochemical performance. The conductivity of MnO₂ is also relatively low. Therefore, MnO₂ was often incorporated into composite materials with electron conductors to enhance the dispersion of MnO₂ and increase the conductivity. One of the typical materials to increase conductivity is graphite.

Another alternative catalytic material is molybdenum sulfide (MoS₂), which is a silvery black solid that occurs in nature as the mineral molybdenite. Because of its high stability, MoS₂ is usually unaffected by dilute acids and oxygen. In appearance, it is relatively similar to graphite. MoS₂ nanoparticles supported on graphite are also considered as an exciting new catalyst for hydrogen evolution on the nitrogenase enzyme.³⁸ However, an inherent disadvantage of this material is its low conductivity and insufficient number of active sites. Yuan et al.³⁹ have used MoS₂ plus CNT composite as catalyst to produce hydrogen in microbial electrolysis cell (MEC) and found that its activity is high. Because of its simple synthetic procedure, and the low cost,⁴⁰ MoS₂ is promising for future MFC studies.

In this study, MnO₂ plus graphite and MoS₂ plus graphite composites with different proportions (1:10, 1:5 and 1:3) are used as catalyst in paints and coated on the surface of the cathode, which is made of stainless steel. The COD values of the MFCs are measured in order to calculate coulombic and energy efficiencies and analyze the effect of wastewater treatment with these catalysts. To optimize the power density of MFC, mixtures of MnO₂ and MoS₂ with different proportions (1:1, 1:2 and 2:1) are used in order to find the optimal value of mixing proportions. Mixing both materials was done because it was observed during our experiments that coatings with MnO₂ had good activity at the beginning but declined over time, while MoS₂ had low activity at the beginning of MFC operation but good activity after some time of operation. It was expected that the combination could lead to improved MFC performance.

The scaling up of MFC with graphite plus MnO₂ composite is also studied in this research. For this purpose, larger MFCs are prepared. The MFCs with dimension of 700 mm × 140 mm were connected in series for the wastewater supply, the anodes have two sides for enlargement of reaction surface (one anode was placed between two cathodes). This concept is also introduced by Suresh et al., but who used two gas diffusion cathodes under different operational modes for MFCs.⁴¹

Experimental

Wastewater and COD Substrate.—The purpose of our study was the examination of the new combined catalyst coatings in real wastewater and to study the first stage of scale up toward commercial scale MFCs. The wastewater with the initial COD value of 250 to 300 mg/L was provided by a municipal wastewater treatment plant in Goslar, Germany. After sometime when the MFC have consumed nutrition contained in the wastewater, a solution of 200 g/L glucose and 200

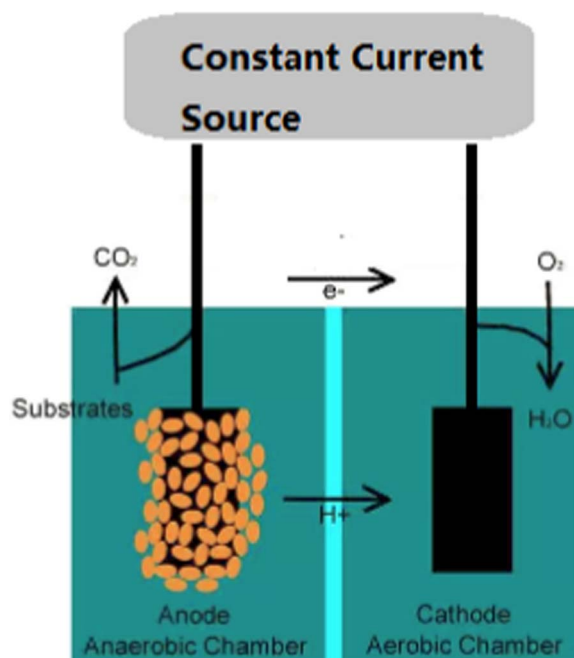


Figure 1. Schematic of the basic elements of a single MFC.

g/L NaAc dissolved in distilled water was used to supply the microorganism with nutrition.

Design of MFC.—Two different sizes of microbial fuel cells were used. A schematic of the smaller cells (150 mm × 150 mm) is shown in Fig. 1. The system was designed to keep the bacteria on the anode separated from the cathode solution and to separate the anaerobic and aerobic compartments also. This is realized by using a membrane or separator. Moreover, the separator should also be used for proton exchange. During the experiments proton exchange membranes were used as separator between anode and cathode compartment of the MFCs (manufacturer: Fumatech Corporation; type: FKE 50). As electrodes a polymer/graphite composite (approximately 85% graphite in an olefinic polymer binder) was used, as it is known that microorganism can settle easily on graphite which is a major compound in these plates. These materials were prepared by Eisenhuth Corporation (Germany) and are also used in other electrochemical reactors like batteries or electrolyzers. The conductive plates can be easily manufactured by polymer processing methods, resulting in low cost. Flat plates with channels for the wastewater flow were used, which is shown in Fig. 2.

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).

Preparation of graphite plus MnO₂ and graphite plus MoS₂ paints for evaluation in laboratory scale MFCs.—For preparation of cathode dispersion, MnO₂ was received by EMD Millipore Corporation in USA (article number 805958), MoS₂ by Metallpulver24 Corporation in Germany (article number 22020) and graphite RA by Eisenhuth Corp. Germany.

Graphite and MnO₂ (or MoS₂) were mixed with the weight proportion of 10:1, 5:1 and 3:1 respectively. As a polymer binder a solution made of 150 mL butanone and 7.5 g celluloid (taken from table tennis balls) is produced. It may be that the use of celluloid from



Figure 2. Construction of our improved anode for usage in laboratory scale MFCs.

table tennis balls seems unusual, but the benefit is that this material is highly flexible and contains no additives which could be harmful for our water environment. In addition the properties (like flexibility) are well regulated by international sports regulations. So reproducibility is guaranteed. The mixture of MnO_2 (MoS_2) and graphite is added into the celluloid butanone solution. 80 ml binder solution was mixed with 17.6 g of graphite catalyst mixture. The components were chosen considering the aspect that no poisonous materials should be used in a water treatment plant. Coating can be done by hand with a paintbrush or an automated spraying machine. In our research, the catalysts are coated by use of a manual paintbrush on the surface of the cathode with an average loading ratio of 0.16 g (catalyst) / g (cathode). 1.4301 AISI 304 stainless steel meshes ($w_{\text{mesh}} = 1.8 \text{ mm}$, $d_{\text{wire}} = 0.32 \text{ mm}$) by Spörl KG Präzisionsdrahtweberei Corporation (Germany) with dimension of $150 \text{ mm} \times 150 \text{ mm}$ are used as cathodes. A sample of a stainless steel cathode with graphite plus MnO_2 composite coating and four in series connected MFCs with stainless steel as cathode carrier material is given in Fig. 3.

Scaling up of MFCs.—To reach the next step in scale up, four MFCs with active anodic area of $700 \text{ mm} \times 140 \text{ mm}$ were designed and constructed in our research. The scaled up MFCs in series are shown in Fig. 4, an insight to the design also.

To enlarge the reaction area of the new design, the anode plates have two sides with channels. These were produced by our project partner Eisenhuth Corporation (Germany). In our research, the catalysts are coated by use of a manual paintbrush on the surface of the cathode with an average loading ratio of 0.16 g (catalyst)/g (cathode). Stainless



Figure 3. Stainless steel mesh with graphite plus MnO_2 composite (left) and in series connected smaller laboratory scale MFCs (right) ($150 \text{ mm} \times 150 \text{ mm}$).

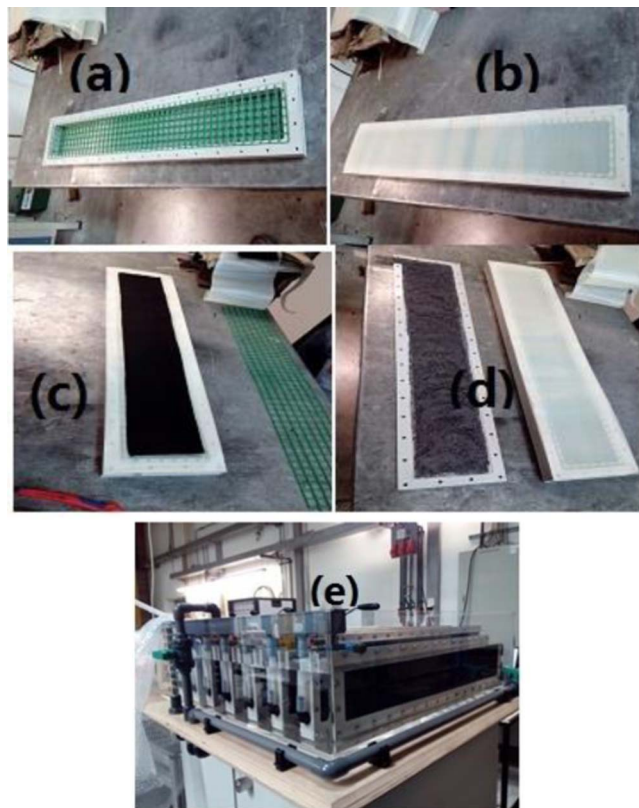


Figure 4. Materials of scaled up MFCs (a) PVC frame for anode plates, (b) Proton exchange membrane, (c) ACN-211 for improving power density, (d) Coated stainless steel mesh with graphite plus MnO_2 composite as cathode, (e) assemble scaled up MFCs.

steel meshes (1.4301 AISI 304; $w_{\text{mesh}} = 1.8 \text{ mm}$, $d_{\text{wire}} = 0.32 \text{ mm}$ for fine mesh and $w_{\text{mesh}} = 3.15 \text{ mm}$, $d_{\text{wire}} = 0.56 \text{ mm}$ for rough mesh) from Spörl KG Präzisionsdrahtweberei Corporation (Germany) with dimension of $700 \text{ mm} \times 140 \text{ mm}$ are used as cathode coated with catalytic composite, which are graphite plus MnO_2 composites with mixing proportion of 10:1. One of the MFCs was constructed with additional graphite felts (ACN-211 by Kynol Corporation, Germany) for further increasing surface area on the cathode to improve power density. Table I shows the technical data of ACN-211. This one was used in our experiments because it had the highest specific surface area. For comparison other available types of carbon felts from the same corporation were also listed in Table I. The surface area of ACN-211 is $1500 \text{ m}^2/\text{g}$ with carbon fiber content of 100%.

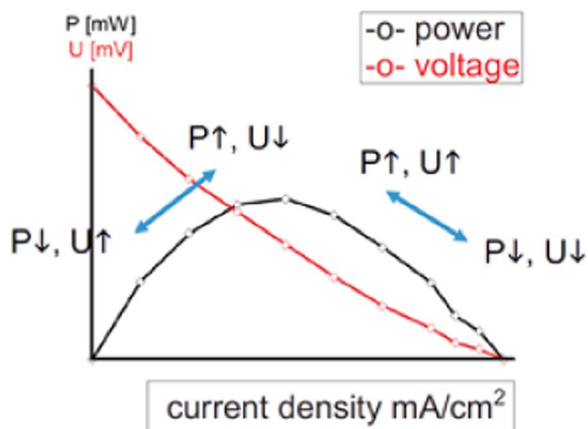
Different cells with different electrode materials and separators were used for comparison, Table II shows the used materials. Furthermore, different membranes were also used for the MFCs, which are FKE-50 with thickness of 0.05 - 0.07 mm and conductivity of 3 mS/cm and FKS-130 with thickness of 0.11–0.13 mm and conductivity of 5 mS/cm (Fumatech Corporation, Germany).⁴²

Table I. Technical data of carbon fiber felts from Kynol Corporation.

| Article No. | Carbon fiber content (%) | Weight (g/m^2) | Apparent thickness (mm) | Specific surface area (m^2/g) |
|-------------|--------------------------|----------------------------------|-------------------------|---|
| ACP-304 | 50 | 50 | 0.2 | 630 |
| STV-505 | 50 | 50 | 0.2 | 700 |
| ACN-157 | 100 | 90 | 1.5 | 1,500 |
| ACN-211 | 100 | 180 | 2.5 | 1,500 |

Table II. Materials used for the different MFCs.

| Cell No. | Membrane (byFumatech Corp.) | Stainless Steel mesh Cathode carrier (by Spörl KG Präzisionsdrahtweberei Corp.) | ACN-211 (byKynol Corp.) |
|----------|-----------------------------|---|-------------------------|
| 1 | FKE-50 | rough/fine | - |
| 2 | FKE-50 | fine/fine | - |
| 3 | FKE-50 | fine/fine | on both sides |
| 4 | FKS-130 | fine/fine | - |

**Figure 5.** Strategy for optimization of MFC power output by software controlled load currents.

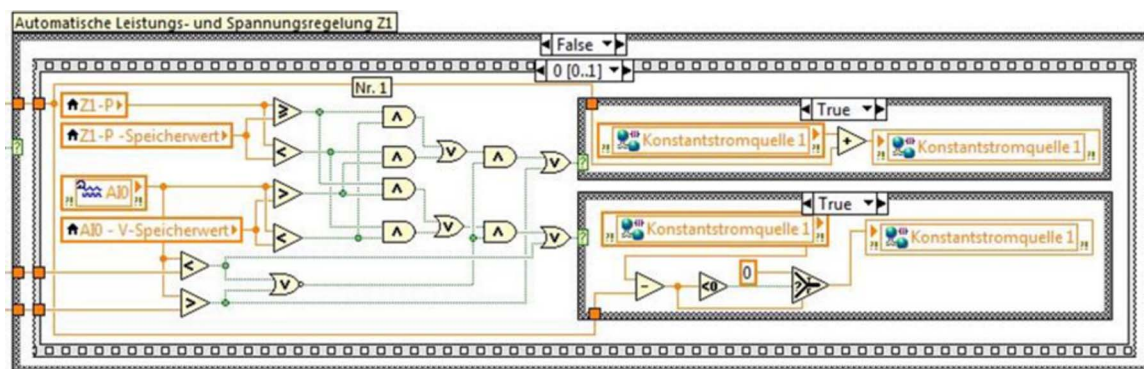
Measurement of power density and MFC-bottleneck identification.—State of the art in MFC research is the use of resistors with fixed values as an electric load. The resistor is needed to allow the microorganism to release their generated electrons. This method works, but is not the best approach to load the MFCs electrically. MFCs are electrochemical reactors with living organism on the electrodes. This results in fluctuations of power density which cannot be forecast. Therefore a fixed resistor does not fit optimal to the variable power output of the MFC. The better the microorganism can give of produced electrons the better they can live and the better the bio-film on the electrodes will develop. Our approach is different from the well-known resistor load. The MFCs are loaded with constant current sources. The current is adapted to the prevailing power capability of the MFC. So the MFCs were loaded individually with different constant currents, each MFC is connected with an own constant current source. Simultaneously the potential was measured. From these data the current density/voltage characteristic and the current density/power density characteristic were calculated on-line by LabView software (National Instruments). These data are not constant over time but change during the operation of a MFC. This

is caused by changing supply with nutrition, varying supply with oxygen and individual development of the microbial film on the electrodes. So it is necessary to measure these data several times a day and adjust the applied load current to the maximum power point in the current density/power density characteristic of each MFC. In Fig. 5 four possible situations are depicted. By comparison of voltage and current of the freshest measurement with the stored data from the previous measurement the status of operation is identified. In the next step the load current is adjusted stepwise toward the direction of the power maximum. The time interval for the measurements can be chosen freely as well as the current increments, so this method can be adapted to different sizes of MFCs. By this approach each MFC was operated at the individual maximum power point in the current density/power density characteristic and a rapid development of the microorganism could be reached leading to a fast power production. Materials with beneficial properties can be easily detected and be used for the development of industrial MFCs. All materials can be compared at the maximum power point this material in combination with the other materials of construction can deliver. The LabView program structure for controlling the constant current values is shown in Fig. 6.

Before the cathode with a catalytic coating is used for a MFC, a MFC with an uncoated stainless steel cathode was set up and the polarization curve was measured by using a reversible hydrogen reference electrode (RHE) as it is shown in Fig. 7. The application of a reference electrode was necessary to determine which electrode limits the power output of the MFC. We adapted a method described in literature, described by He and Nguyen.⁴³ During assembly of the MFC the membrane was left larger than the surface area of the MFC. The membrane outside the cell was immersed into a beaker filled with diluted sulfuric acid. In the beaker a commercial hydrogen reference electrode (Gaskatel company, Kassel, Germany) was inserted. So by the membrane a conductive ionic connection between the MFC and the reference electrode was created. With this arrangement is it possible to measure anode and cathode potentials individually not disturbing the inner construction of the MFC with additional measuring electrodes and capillaries. Simultaneously the cell voltage was measured. By rising the load current with the constant current source it could be observed that the cell voltage begins to drop when the cathode voltage begins to change. This indicates that the cathode is the power limiting electrode in a MFC. This is depicted in Fig. 8.

Coulombic and energy efficiency.—*Coulombic efficiency.*—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. One of the most important parameters to evaluate the efficiency of MFC is coulombic efficiency, which is defined as follows,

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

**Figure 6.** Logic flow sheet for the program routine in LabView software to adjust the MFCs to individual maximum power production.

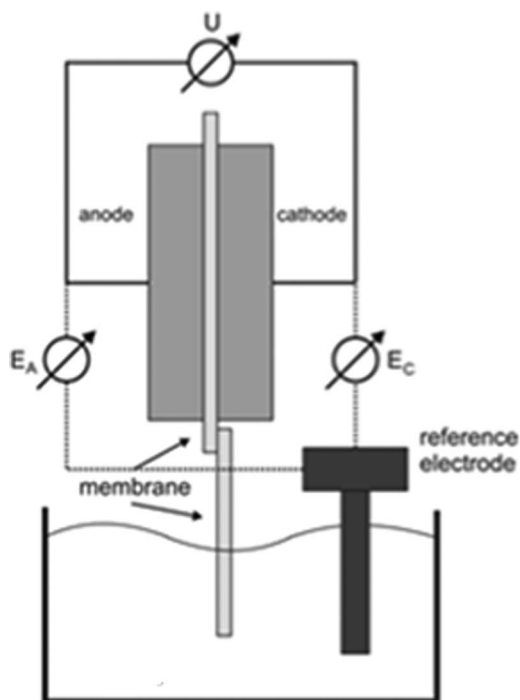


Figure 7. Application of a reference electrode (RHE) to measure anode and cathode potentials individually.⁴³

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

$$\eta = \frac{M \int_0^t I dt}{FbV_{An}\Delta COD} \quad [2]$$

With M as the molar mass of oxygen ($32 \text{ g} \cdot \text{mol}^{-1}$); F as the Faraday constant $96,485 \text{ C} \cdot \text{mol}^{-1}$; I as the current of MFC; V_{An} as the volume of anode, b as the quantity of exchanged electrons of oxygen and ΔCOD as the differential of COD value in MFC system.

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,

$$\eta_E = \frac{E}{E_{max}} \eta \quad [3]$$

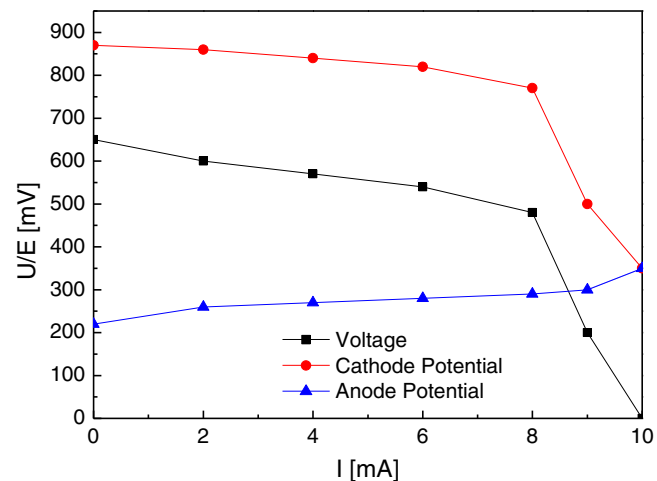
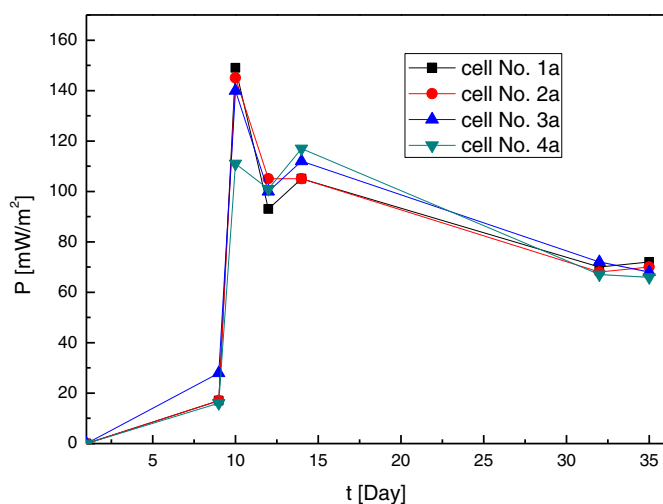


Figure 8. Polarization curve of a standard MFC with uncoated stainless steel cathode.

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

Start-up behavior of MFCs with graphite plus MnO_2 paint.—

Four small MFCs (cell No.1a, 2a, 3a, 4a; each with 225 cm^2 active area) with graphite plus MnO_2 paint with the graphite plus MnO_2 weight proportion of 10:1 were connected in series with the wastewater supply. Their start-up behaviors and long term performance were evaluated (Fig. 9, left). The depicted data are the maximum power point data determined by the LabView control system. The data in Fig. 9 suggested that the power densities increased slightly with time within nine days. However, the power densities increased rapidly and reached relatively high values (for cell No.4a 110 mW/m^2 , for cell No.1a, 2a and 3a 150 mW/m^2) at the 10th day and then tended to

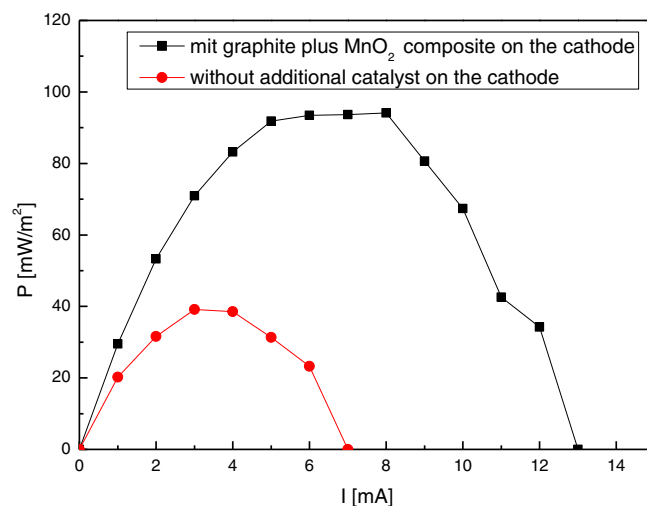


Figure 9. Power density development over time (left) and output power densities of an improved and unimproved MFCs after 2 weeks (right).

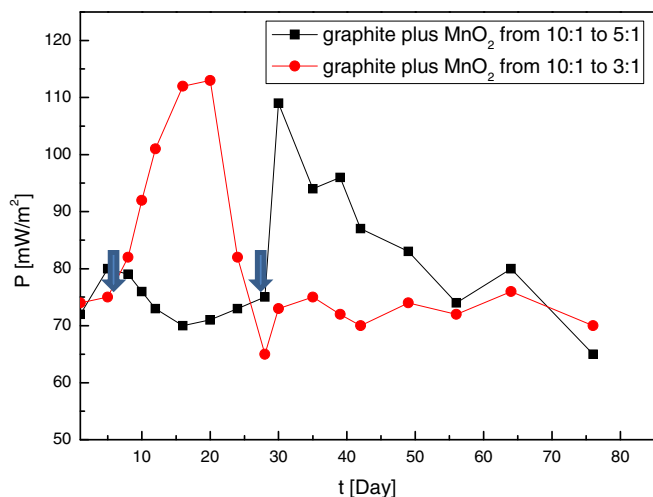


Figure 10. Long term performance of a cathode with graphite plus MoS₂ paints. Arrows show cathode installation from 10:1 to 5:1 and 10:1 to 3:1.

fluctuate around a value of 70 mW/m². This behavior that the power densities develop over longer times with fluctuations is quite common in MFCs. Zhang et al.⁴⁴ have used carbon nanotubes (CNT) with coated MnO₂ as cathodic catalyst and achieved an optimal power density of 200 mW/m² by using anaerobic sludge collected from the Liede municipal wastewater treatment plant (from Guangzhou, China), which is slightly higher than that obtained in our experiments. But they used CNT as carrier, which is much more expensive than graphite. A cathode without a catalyst for the oxygen reduction reaction in our experiments reached only a power density of about 40 mW/m². The power density could be improved by more than 50 mW/m² (Fig. 9, right) by the application of MnO₂ as a catalyst, this is an increase of a factor of more than two. Suresh Babu Pasupuleti et al. have developed membrane-free single-chamber cell by using RuO₂ as coating on the surface of the Ti cathode.⁴⁵ A maximal power density of only 70 mW/m² was achieved at 27th day during the long term performance, which is lower than that of MFCs in our research. In addition the application of noble metals as catalysts in MFCs is not efficient regarding costs. This demonstrates that a low cost MnO₂ catalyst can play an important role in improving the power density generation of MFCs by increased electrochemical cathode activity.

Long term performance of graphite plus MnO₂ paints with higher proportion of MnO₂.—To study the influence of catalytic paint composition we varied the graphite:MnO₂ ratio. The loading with catalytic paint on the electrodes was kept constant. Higher MnO₂ loadings were reached. Fig. 10 shows the long term performance of MFCs with graphite plus MnO₂ paints of 5:1 and 3:1. The arrows in Fig. 10 show the time, in which graphite plus MnO₂ composites with new graphite plus MnO₂ proportions (5:1 and 3:1) are used. The data suggested that after reaching the best performance, the power densities of MFCs descended rapidly. The best performances were achieved in MFCs with graphite plus MnO₂ proportion of 5:1 and 3:1 at 30th and 20th day respectively, whose values are 109 mW/m² and 114 mW/m² respectively. In comparison to the performance of graphite plus MnO₂ composite with graphite plus MnO₂ proportion of 10:1, the power densities of graphite plus MnO₂ composites with graphite plus MnO₂ proportion of 5:1 and 3:1 are relatively low, showing that higher proportion of MnO₂ shows no effect on improving the power density of MFCs.

Long term performance of graphite plus MoS₂ paint.—The long term performance of MFCs with graphite plus MoS₂ paint of 10:1 ratio is given in Fig. 11. The arrow in Fig. 11 shows the time, in which graphite plus MoS₂ paint was installed and used. The data suggested that the power density of MFC increased after using graphite

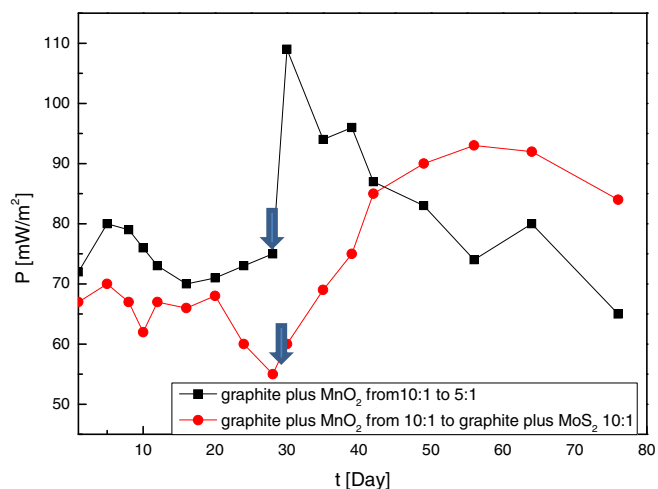


Figure 11. Long term performance of a cathode with graphite plus MnO₂ paints. Arrows show cathode installation from 10:1 to 5:1 and from 10:1 to MoS₂ paint (10:1).

plus MoS₂ paint. Despite of the relatively low power density at 30th day, the best performance is achieved at 65th day with the value of 90 mW/m². After reaching the best performance, the power density fluctuated with the value of 85 mW/m². Comparing with graphite plus MnO₂ composite, the power density of graphite plus MoS₂ composite increased much more slowly with time and its value is also relatively lower. However, the graphite plus MoS₂ composite shows a much higher stability than graphite plus MnO₂ composite. Therefore, in order to achieve a higher power density and stability contemporarily, MnO₂ and MoS₂ should be mixed with a certain proportion.

Performance of MFCs with different MnO₂/MoS₂ mixing proportions.—The combination of different catalysts (MnO₂ and MoS₂) is necessary for further improvement of power density. The power density performance of MFCs with different MnO₂ plus MoS₂ proportions is shown in Fig. 12. The data suggested that the MFC with mixed catalysts with graphite plus MnO₂ plus MoS₂ proportion of 20:1:1 possessed the highest power density during experiments (125 mW/m² at 5th day). It can be seen in Fig. 12 that the power density of MFC with mixed catalysts with graphite plus MnO₂ plus MoS₂ proportion of 30:1:2 possessed the value of 85 mW/m² at the

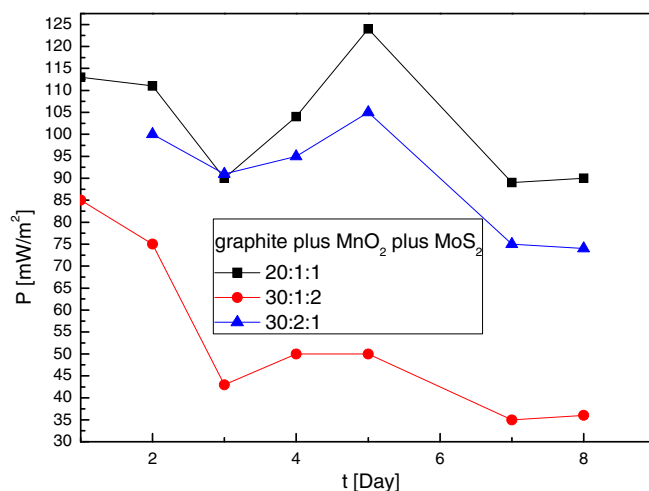


Figure 12. Performance of MFCs with cathodes based on the combination of MnO₂ and MoS₂ proportions as indicated.

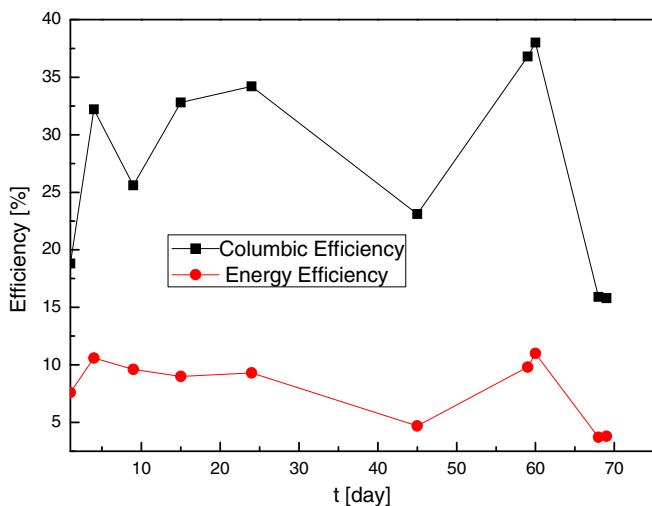


Figure 13. Average coulombic and energy efficiency of the whole MFC stack during long term operation.

beginning and descended rapidly after starting operation. The power density fluctuated around a value of 35 mW/m^2 after the 7th day. However, comparing with the MFC with mixed catalysts with graphite plus MnO_2 plus MoS_2 proportion of 30:2:1, the power density of MFC with graphite plus MnO_2 plus MoS_2 proportion of 20:1:1 shows a better performance, showing that 20:1:1 is the optimal mixing proportion in our experiments.

Coulombic and energy efficiency.—The coulombic and energy efficiencies of the whole MFC system (all cells together) are calculated by measured COD values. Fig. 13 shows the long term performance of coulombic and energy efficiencies. The data suggested that the coulombic efficiency fluctuated between 20% and 35% from 1st day to 45th day, while the energy efficiency fluctuated between 5% and 10%. The best performances are achieved at 59th (36.8%) and 60th (38%) day, at which the graphite plus MnO_2 composites (5:1 and 3:1) and graphite plus MoS_2 (10:1) composite were used. However, because of decrease of power density after achieving the best performance, both the coulombic and energy efficiencies decreased to 15.8% and 3.8% respectively.

Start-up behavior of scaled up MFCs.—Different cell components and material combinations were tested with the best $\text{MnO}_2/\text{MoS}_2$ catalyst determined in the smaller laboratory cells. Fig. 14 shows the start-up behavior of MFCs with larger dimensions, from cell No. 1b to 4b. According to Table II, cell No. 1b is constructed with a rough and a fine steel mesh, while cell No. 2b is constructed with two fine steel meshes on both sides of the anode. It can be seen in Fig. 14 that the power density of cell No. 1b increased with time at the beginning and fluctuated around a value of 75 mW/m^2 after ten days. The data suggest that the power density of cell No. 2b increased continuously until the 39th day and then fluctuated around a value of 125 mW/m^2 . The best performance is achieved at 39th day with the value of more than 200 mW/m^2 , whose main reason is that a fine stainless steel mesh possesses a relatively large surface area (Table I), which is beneficial for both coating process and cathodic reaction. The similar phenomenon is also observed by Suman et al., who used carbon felt and stainless steel mesh assembly as cathode.⁴⁶ According to Table II, the difference between cell No. 2b and 3b is that cell No. 3b is constructed with additional graphite felts on the stainless steel cathode. It can be seen in Fig. 14 that the power density of cell No. 3b increased with time from 1st day to 37th day and possessed a higher power density than cell No. 2b. However, the power density of both cells No. 2b and 3b decreased after 37 days, whose main reason

is that there was not enough substrate (laboratory failure!) to support the power densities of MFCs. It can be seen in Fig. 14 that the power density of cell No. 3b is still higher than that of cell No. 2b after decrease, showing that an additional graphite felt plays an important role in improving the performance of catalytic coated stainless steel mesh cathodes. According to Table II, cell No. 2b and 4b were equipped with different proton exchange membranes (FKE 50 and FKS 130 by Fumatech Corp.). As it is mentioned in chapter 2, the FKE-50 membrane possesses thickness of 0.05–0.07 mm and conductivity of 3 mS/cm , while FKS-130 possesses a thickness of 0.11–0.13 mm and conductivity of 5 mS/cm . The data in Fig. 14 suggested that the power density of cell No. 4b increased with time during the first 37 days. The best performance is achieved at the 37th day with the value of 195 mW/m^2 . It can be seen in Fig. 14 that the power density of cell No. 4b was higher than that of cell No. 2b during the first 37 days, showing that the membrane seems to influence power density of the MFCs. But considering the high conductivity of the membranes in comparison to the low conductivity of the wastewater a real effect of membrane conductivity seems not probable. However, the power density of cell No. 4b decreased after achieving the best performance and fluctuated around a value of 100 mW/m^2 , which is similar with cell No. 3b. The main reason is also lacking of substrate in anode chamber as described above. However, comparing with the power density of cell No. 2b, the power density of cell No. 4b is still higher at 51st day. By these experiments the best combination of the materials used in our research was found. The combination graphite plus MnO_2 plus MoS_2 in proportions of 20:1:1 as a coating on fine stainless steel mesh combined with carbon felt ACN 211 resulted over longer times in the most satisfying performance.

Reached Status and Outlook

By our investigation a good catalyst combination for coating stainless steel cathodes with satisfying long time performance was reached. In order to study the influence of coating methods on power density of MFCs in future work different coating methods (by hand or spray machine) should be used, in combination with new catalyst-ratios. Using a dispersion mill for the paint preparation will improve paint quality so that it can be applied by an automated spraying machine. This step is necessary to be able to prepare electrodes on an industrial scale in a short time. With the test of two MFC dimensions the first step to scale up to commercial cell dimensions was done. The cells with $700 \text{ mm} \times 140 \text{ mm}$ were used to demonstrate MFC power production ability during the IFAT fair, Munich, July 2016. It was the biggest MFC which was operated in Germany with real wastewater and could demonstrate continuous power production shown by a light

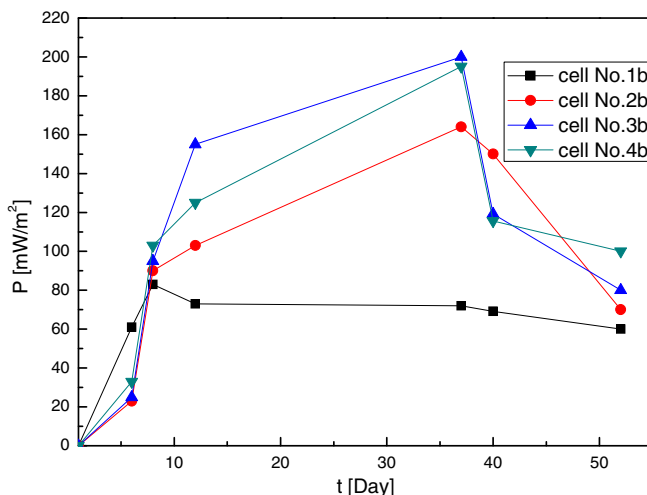


Figure 14. Start-up behavior of scaled up MFCs.

emitting diode powered by DC/DC converters which received their electricity from the MFCs. The next step is implementation of bigger cells into a real wastewater plant at Goslar, Germany. This plant is under construction.

Conclusions

A MFC with uncoated stainless steel cathode is firstly constructed and the polarization curve as well as the individual electrode potentials is measured by using a reversible hydrogen reference electrode (RHE) which does not disturb the inner construction of the MFC. The data reveal that the voltage of MFCs descends with increasing load current. When the load current reaches a value too high for the cell to deliver the cathode potential descends rapidly showing that the cathode is the limiting factor for MFC power. Therefore, it is necessary to enhance the cathode performance by adding an electrocatalyst on the cathodes surface.

A low cost MnO₂ catalyst can play an important role on improving the power density generation of MFCs by increased electrochemical activity on the cathode. A cathode without a catalyst for the oxygen reduction reaction reached only a power density of about 40 mW/m² in our experiments with real wastewater. The best performance of MFC with graphite plus MnO₂ composite (10:1) was more than 100 mW/m². The best performances of graphite plus MnO₂ composites with 5:1 and 3:1 are achieved at 30th and 20th day respectively, whose values are 109 mW/m² and 114 mW/m² respectively. Comparing with the performance of graphite plus MnO₂ composite with 10:1, the power densities of graphite plus MnO₂ composites with 5:1 and 3:1 are relatively low, showing that higher proportion of MnO₂ shows no effect on improving the power density of MFCs. An explanation may be that the higher concentration of the not conducting catalyst lowers the paint conductivity. Comparing with graphite plus MnO₂ paint, the power density of graphite plus MoS₂ paint increased much more slowly with time and its value is also relatively low. However, the graphite plus MoS₂ paint shows a much higher stability than graphite plus MnO₂ paint. Therefore, in order to achieve a higher power density and stability over long operation times, MnO₂ and MoS₂ should be mixed together with a certain proportion.

The power density performance of MFCs with different MnO₂ plus MoS₂ proportions is studied and the data suggested that the MFC with mixed catalysts with MnO₂ plus MoS₂ proportion of 1:1 possessed the highest power density during experiments. The power density of MFC with mixed catalysts with MnO₂ plus MoS₂ proportion of 1:2 possessed the value of 85 mW/m² at the beginning and descended rapidly after the construction. Comparing the MFC with mixed catalysts with MnO₂ plus MoS₂ proportion of 2:1, the power density of MFC with MnO₂ plus MoS₂ proportion of 1:1 shows a better performance, showing that 1:1 is the optimal mixing proportion.

For the scaled up MFCs, the best performance of cell No.2b is achieved with the value of more than 200 mW/m², which is higher than that of cell No.1b with a rough stainless steel mesh. So a fine stainless steel mesh should be used. In addition a fine mesh is easier to handle during assembly. The power density of cell No.3b with graphite felts ACN-211 increased with time from 1st day to 37th day and possessed a higher power density than cell No.2b. However, the power density of both cell No.2b and 3b decreased after 37 days, whose main reason is that there was not enough substrate to support the power densities of all MFCs. In addition we observed a plugging of the graphite felts by microbial films, which may contribute to power decline. The power density of cell No.3b is still higher than that of cell No.2b after decrease, showing that graphite felt plays a role in improving the performance of catalytic stainless steel coated mesh. Considering this, the additional costs and the observed trend to plugging we cannot recommend the application of felt electrodes in real wastewater. Considering the membrane it is obvious that the membrane has a slight influence on power performance. As membranes

are expensive MFC components the cheapest membrane which is available should be used.

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