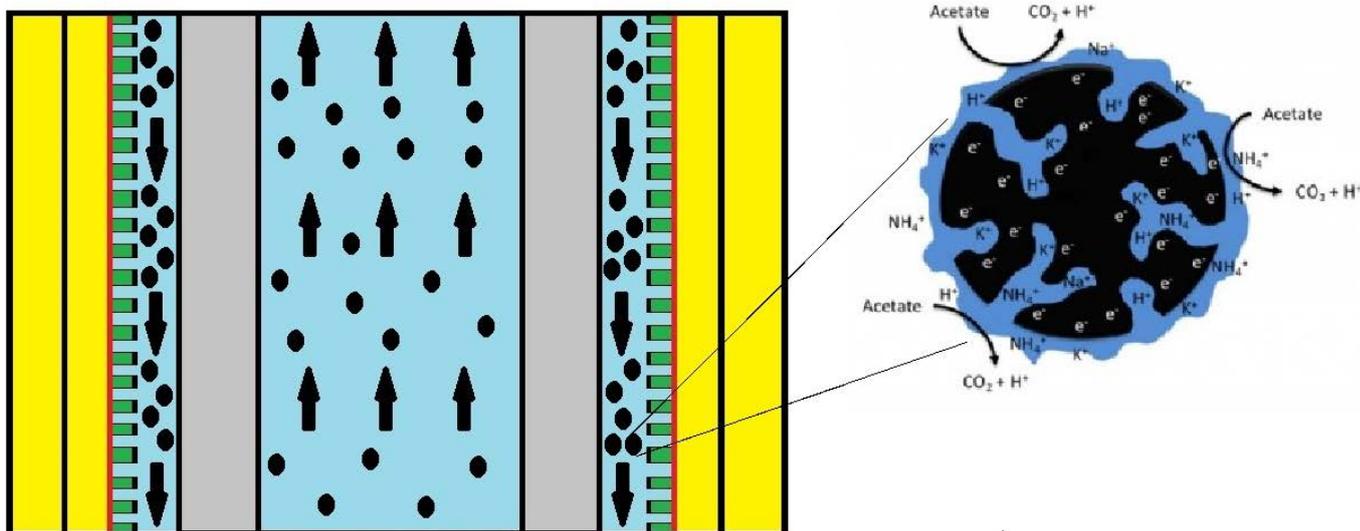


Discovering the potential of a Capacitive Moving Bed Microbial Fuel Cell



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Abstract

Domestic wastewater contains a biodegradable organic fraction that can be used as a resource for the generation of renewable energy. A promising new technology that can convert this organic fraction directly into electricity while also treating the wastewater, is the Microbial Fuel Cell (MFC). Unfortunately the present day MFC still has some disadvantages like a low power output, high price and problems regarding scalability. The Capacitive Moving Bed Microbial Fuel Cell (CMB-MFC) attempts to overcome these challenges, with a major focus on increasing the power output.

However, it is not very clear how the different design parameters of the CMB-MFC relate to each other and affect the overall performance of the reactor. Therefore the goal of this thesis is to investigate these relationships and use this information to see how the performance of the reactor can be optimised. The research question of this thesis is therefore: *How do the design parameters affect the overall performance of the capacitive moving bed reactor?*

To answer the research question, a model is made in Excel, in which the dimensions of the reactor, the physical characteristics of the materials of the reactor and the characteristics of the carbon granules that are used in the reactor are inserted. Equations are used to calculate the performance parameters of the reactor, expressed in current (density) and power (density) output. These output values are compared with similar reactor systems to interpret the calculated values and investigate how well the CMB-MFC performs.

The calculations from the model show that a higher power output can be reached with the CMB-MFC. The current density is estimated to be 46.1 A/m^2 for the GAC granule and 87.4 A/m^2 for the PK granule, which are more than one order of magnitude larger than similar reactor systems. The power densities are calculated to be 18.4 W/m^2 for the GAC granule and 12.3 W/m^2 for the PK granule, which are the highest calculated power density values in a MFC to date (normalised to electrode area).

With the performance results of the CMB-MFC that are much higher than similar reactor systems, the CMB-MFC appears to be the promising new step in the development of MFC technology. However, the overall performance of the reactor depends on many input variables, of which some input values like the anolytic conductivity are not exactly clear. Therefore it is recommended to measure these input values to see if the measured values match the assumed values that are used in the model.

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Introduction

On Saturday the 12th of December 2015 history was made when the delegations of 195 countries reached a significant agreement on the new climate treaty at the U.N. Climate Change Conference in Paris. One of the key results of the conference was the agreement of limiting the global temperature increase to a maximum of 2 degrees Celsius (Center for Climate and Energy Solutions, 2015). Since the increase of global temperature is a result of the rise of the global levels of carbon dioxide, the total global emissions of CO₂ should be confined to keep the average global temperature below the 2 degrees limit (IPCC, 2007). This requires a transition to a society in which energy is produced by renewable energy resources, as our current energy system relies on fossil fuels which emit large amounts of carbon dioxide. An example of a renewable energy resource that can be used in addition to sun and wind energy, is the biodegradable organic fraction of wastewater (McCarty, 2011).

The chemical energy of this organic fraction can be converted into electrical energy by using a novel technology called a Microbial Fuel Cell (MFC), a device that converts the organic substrate directly into electricity by using electroactive bacteria as catalysts. Although the direct conversion of the organic fraction to electrical energy makes the MFC technology very promising, there are still many challenges to overcome to make the MFC economically competitive. Examples of these challenges are the areas of the low power output, the scalability and high costs of the MFC (Logan, 2006).

The parameters that are used to express the power output are current density and power density. The current density can be increased by increasing the conversion rate, since the current density is linked to the conversion rate of the organic matter. The conversion rate can be increased if three-dimensional electrodes are used that provide a higher surface area for the electroactive microorganisms that convert the organic substrate to electricity. One type of suitable material often used for the three-dimensional electrodes is activated carbon granules. These granules have the additional advantage that they can act as a capacitor: they can store the energy that is released by the electroactive biofilm in one location and discharge this energy at another location. (Frackowiak, 2001). This intermittent charging and discharging of the activated carbon granules enables the opportunity to construct a MFC in which the granules are charged in a so called charging column and discharged in a discharging cell that houses the anode, cathode and membrane. This principle of separate charging and discharging of activated carbon granules has been tested in a so called fluidized bed reactor (Deeke, 2015).

The lessons learned during the research with this reactor are used to design a new reactor in which the previously reached current densities are improved. To date, it is not entirely clear how the different design parameters affect the overall performance of this Capacitive Moving Bed Microbial Fuel Cell (CMB-MFC) and what the highest power output of the reactor can be. Therefore this thesis investigates and models the relationships of the different design parameters to clarify how the performance can be optimised. The following research question is posed accordingly:

Research Question

How do the design parameters affect the overall performance of the capacitive moving bed reactor?

Subquestions

- *What is the estimated current for a maximal power output?*
- *How is the performance affected by the conductivity of the anolyte?*
- *How is the performance affected by the discharge time?*
- *How is the performance affected by the width of the flowchannel?*

Requirements and Constraints

The eventual goal for the development of Microbial Fuel Cells is to build a system that is an overall improvement of the current wastewater treatment technologies (for domestic and industrial wastewater treatment). At this moment a conventional domestic wastewater treatment plant (WWTP) uses the aerobic activated sludge process in the secondary stage of the treatment process. The idea is to replace this activated sludge process in the secondary stage with MFC-technology. However, this can only be done if the MFC has an overall performance and cost that are at least as good and preferably better than the current systems. Therefore different requirements (or constraints) are drafted, which set and constrain the direction of the development of MFCs. These are technical, environmental, financial and societal requirements.

For the technical aspects, the MFC is developed with the aim of harnessing the energy inside the organic fraction of the wastewater and thereby producing energy, instead of consuming energy in the treatment process. The MFC should be able to be manufactured with the currently available materials and production technologies. When the MFC is installed in a WWTP, it should be able to handle the maximum flow rates of the plant. The MFC should also be user-friendly regarding the operation of the system. For the environmental aspects, the effluent of the WWTP has to meet the effluent standards of the EU Water Framework Directive. So if the MFC-system of the overall WWTP contributes to the reduction of nitrogen or phosphorus or not, the effluent of the WWTP should at least meet the European standards. For the financial aspects, the overall cost of the MFC, which consists of construction and operational costs, should minimally be the same as the overall costs of the current systems. In reality, the MFC will only be installed if the overall cost are (a lot) cheaper than the current systems. Regarding the societal aspect, the average person will probably not perceive a difference if conventional aerobic systems are replaced with MFC technology. The only perceivable difference might be a slight reduction of the price that civilians pay to the water boards (who are responsible for the treatment of wastewater).

At this moment, the MFC is in the early stage of development and is still far away in replacing the current wastewater treatment systems. Therefore the main focus and aim of the new capacitive moving bed reactor that is studied in this thesis, is to have a higher performance than similar systems. The performance of the capacitive moving bed reactor is measured in current (density) and power (density). The major actors and institutions involved in this early stages of the development of the MFC, are Universities like Wageningen UR and research institutes like Wetsus. If the MFC becomes an economically viable technology, technology companies will be involved in to build MFCs on a larger scale. The water boards will also be involved when the MFC technology is installed in the wastewater treatment plants.

Methodological Design

To answer the research question, a literature study is made which explores different wastewater treatment systems and the MFC technology. The challenges of the current MFC systems are emphasised, whereafter the design choices of the capacitive moving bed reactor are given that are made to tackle these challenges. Subsequently the Excel Model is described, which is made to calculate the performance of the capacitive moving bed reactor. In the research results the actual performance data of the reactor is given. A part of these results is a description of the influence that different design parameters have on the performance of the reactor. The thesis is finalized with a conclusion that summarizes the most important results, a discussion to put these results into perspective and recommendations for further research.

Theoretical Background

One of the areas in which an energy transition is needed, is the water industry. In developed economies, the water industry uses between 3 and 5 percent of the generated electricity. A major part of this energy is used for the treatment of domestic wastewater, which is normally done via aerobic activated sludge treatment and anaerobic sludge digestion. This process uses on average 0.6 kWh to treat 1 m³ of wastewater, of which about half of the energy is used for the aeration of the bioreactors of the treatment plant (Curtis, 2010). However, the biodegradable organic fraction of the wastewater contains 1.23 kWh/m³ of energy, so there is an energy potential in the wastewater which presents the opportunity to transform wastewater treatment plants from energy consumers into net energy producers (McCarty, 2011). The two potential routes for this transformation are novel anaerobic treatment technologies and microbial fuel cells (MFCs).

Anaerobic Treatment

In contrast to aerobic water treatment plants, which consume oxygen to convert the biodegradable organic fraction in wastewater to carbon dioxide and biomass (sludge), anaerobic systems convert the organic material to methane and carbon dioxide without the need for oxygen. So aerobic reactors use energy for the aeration of the reactors, while anaerobic reactors release energy which is stored in the methane. Compared to the aerobic process, only a small part of the organic fraction of the wastewater is converted to biomass (sludge) in the anaerobic process. Therefore anaerobic reactors are smaller and have a higher loading rate than aerobic reactors. With the developments of anaerobic technology in the past 50 years, it is now possible to fully treat domestic wastewaters anaerobically, especially in countries with a warm climate (Lettinga, 1983).

However there are also disadvantages to anaerobic treatment. Anaerobic reactors need a high organic loading rate (COD) and high temperatures (between 30 and 40 degrees Celsius) for an optimal performance and are therefore not always the best solution for the treatment of wastewater with low organic concentrations in a temperate climate (with temperatures between 0 and 25 degrees Celsius). The biogas consisting of methane and carbon dioxide that is released by the anaerobic reactors first needs to be treated, since it can also contain corrosive and toxic gasses like hydrogen sulphide. Although this methane can be used for cooking and heating, it is more useful for other applications when it is converted to electricity by combusting it in generators. This is not a very efficient process, so only about 30 to 40% of the energy is converted to energy, while the rest of the energy is converted to heat (McCarty, 2011).

An approach that makes the overall process more efficient, is the use combined heat and power (CHP) systems (cogeneration) in which the waste heat is also used (for example for the heating of the anaerobic reactor). However, according to the U.S. Environmental Protection Agency (EPA), the minimal size of a wastewater treatment plant in which cogeneration is efficient, is a plant with a total influent flow rate greater than 19000 m³/day (EPA, 2007). Therefore, there is a demand for a technology that can generate electricity from (smaller) wastewater treatment plants more efficiently. One potential technological system that can fulfil this need, is the Microbial Fuel Cell.

Microbial Fuel Cells

The disadvantages of anaerobic treatment can be overcome by using a Microbial Fuel Cell (MFC). A MFC is a bio-electrochemical system that directly converts the organic material in the wastewater to electricity. The system consists of an anodic compartment with an anode placed in anaerobic anolyte and a cathodic compartment with the cathode placed in aerobic catholyte. These compartments are separated by a cation exchange membrane. The wastewater enters the anodic compartment, in which electrochemically active bacteria oxidise the biodegradable organic fraction and transfer the released electrons to the anode. The electrons flow from the anode (the negative terminal) via the load to the cathode (the positive terminal), see Figure 1 (Mokhtarian, 2013). The cations, which are also released during the conversion of organic matter, flow via a membrane to the cathode (Logan, 2006).

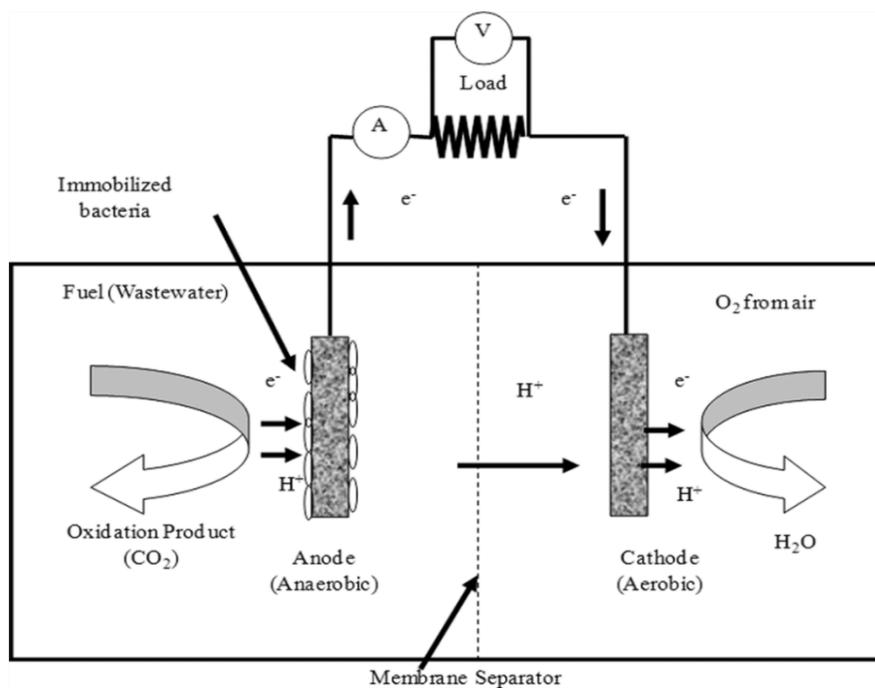
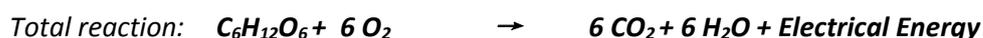
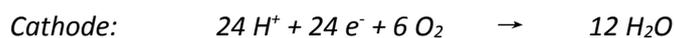


Figure 1 - Operating principles of a MFC

In this process, carbon dioxide is produced in the anodic compartment and water is produced in the cathodic compartment when the H^+ ions combine with the oxygen in this compartment. The overall reaction is illustrated in Equation 1 with glucose as an example for the organic substrate (Pham, 2006).



There are many differences between the MFCs that are currently being developed. There is a variety in the designs and configurations of the MFCs (flat plate or tubular configuration), the size of the reactors (ranging from 1 to 4900 mL anode compartment), the materials that are used for the anode and cathode (like graphite rod, plate, felt or granules and electrocatalytic materials like polyanilins/Pt composites), but also for the materials used for the membrane (a plain salt bridge, Nafion or Ultrex).

Other differences are found in the operating conditions (the temperature, pH and operation time), substrates (glucose, acetate, lactate, wastewater), catholyte used for the MFC (like ferricyanide ($K_3[Fe(CN)_6]$)) and microbial communities (axenic and mixed cultures) (Logan, 2006).

The Microbial Fuel Cell has many advantages over other wastewater treatment technologies. The first advantage is the direct conversion of the organic material to electricity, which apparently enables a higher conversion efficiency compared to anaerobic treatment. Since the electricity is generated directly in MFCs, no off-gas treatment is needed. Another advantage is that MFCs operate more efficiently at lower temperatures and organic loading rates than anaerobic reactors. The (small) electrical output of an MFC is also more useful than same energy output in the form of methane and therefore the MFC can be used for a greater diversity of applications (Rabaey, 2005).

However, before the MFC technology can be implemented commercially, it has to overcome three challenges to make it economically competitive. The first challenge is the volumetric power density. The volumetric power density of most MFCs is currently in the range of 1 to 200 W/m³, which is too low to be competitive with anaerobic treatment, that has a volumetric power density in the order of 1000 W/m³ (Arends, 2012). The highest power densities that have been achieved with a MFC were 3.6 W/m² (Rabaey, 2003) when normalized to electrode area and 1010 W/m³ when normalized to total reactor volume (Fan, 2007). However these reactors were on the millilitre scale (45 mL for the reactor of 3.6 W/m² and 6 mL for the reactor of 1010 W/m³ output). The second challenge are the costs of the MFC. The electrodes and membranes are expensive components, which makes MFCs about 800 times more expensive than anaerobic systems (Rozendal 2008). The third challenge for successful application of MFCs is scalability: since wastewater is not very conductive, the electrodes have to be spaced very close to each other (in the millimetre range) to prevent voltage losses and thus power losses. This close spacing of the electrodes impedes a high flowrate of the wastewater and therefore the opportunity to scale up the MFC (Janicek, 2014). So to summarize: the performance of the present day MFC is too low, the overall system is too expensive and unsuitable for large scale application.

Before a MFC can be brought to the market successfully to compete with other conventional aerobic and anaerobic treatment systems, the disadvantages have to be resolved. Therefore breakthroughs are needed that address the volumetric power density, the total cost of the reactor and the challenges regarding scalability of MFCs.

Capacitive Moving Bed Microbial Fuel Cell

In the endeavour to overcome the challenges regarding Microbial Fuel Cells, a new type of MFC has been designed, built and tested. This new reactor is called a Capacitive Moving Bed Microbial Fuel Cell (CMB-MFC). The design of the new reactor attempts to resolve the previously given disadvantages of the MFC. The major focus is on increasing the power (density) output, but improving the scalability and decreasing the costs are also important factors for the new reactor.

Volumetric Power Density

The power that is produced by the reactor, is the product of the voltage (V) and the current (I). To maximize the power, the product of voltage and current has to be maximised. The voltage is determined by the type of conversion reactions of the substrate and bacteria in the reactor. This reactions restrict the voltage to a maximal theoretical limit of 1.2 V (Rabaey, 2005). However, due to overpotential losses at the electrodes and losses due to electrolyte resistance, the effective voltage produced in MFCs is much lower, normally in the order of 0.4 V. So to maximize the voltage, these losses have to be minimised and therefore the most optimal electrodes and membranes have to be selected and the distance between the electrodes have to be minimised (Rabaey, 2005).

The relation between maximum cell voltage and losses is given in Equation 2, in which (E_{cell}) is the voltage over the load, (E^0) is the maximum theoretical cell voltage, (η_a) and (η_c) are the voltage losses at the electrodes and ($I \cdot R$) represents the voltage losses due to the internal resistance of the electrolyte (Rabaey, 2005).

$$E_{cell} = E^0 - \eta_a - \eta_c - I \cdot R \quad (2)$$

Since it is not possible to increase the voltage beyond the maximal theoretical limit, but only to minimize the losses related to the voltage, the focus for increasing the power of the MFC lies in minimizing the internal resistance losses and increasing the current output of the MFC. As the current depends on the conversion rate of the substrate, the conversion rate has to be increased to increase the current. In order to increase the conversion rate, the surface area of the electrodes on which the electrochemically active bacteria grow has to be increased.

A cost-effective way to strongly increase the surface area of the electrodes is by using granular materials like activated carbon or graphite granules (Deeke, 2012). The electrochemically active bacteria form a biofilm on the outside of these granules and convert the substrate to electrons and cations of which the electrons are later transferred to the anode, while the cations flow via the membrane to the cathode of the MFC. An additional advantage of activated carbon granules is that they can store the energy (both the electrons and cations) inside the pores of the granule. This property is enabled by the high specific surface area (SSA) of the pores inside the granules. The electrons and cations form an electric double layer (EDL) on this surface area of these pores and thereby store the energy inside the granule as can be seen in Figure 2 (Deeke, 2015).

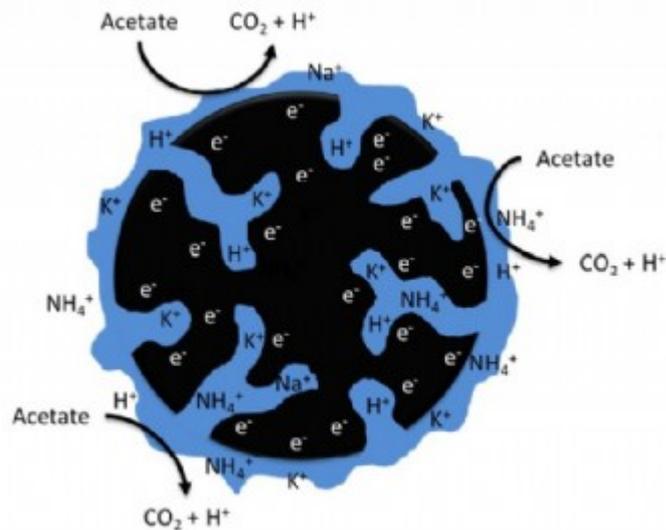


Figure 2 – Capacitive granule with electro-active biofilm and electric double layer inside the pores

This storage capacity enables the opportunity to use the activated carbons as capacitors and charge / discharge the granules at different time or place. The principle of separate charging and discharging of activated carbon granules has been shown in a so called fluidized bed reactor (Deeke, 2015). This reactor had a charging column in which activated carbon granules were charged and a separate discharging cell (with an anode, cathode and membrane) in which the granules were discharged when the granules passed through the discharge cell as can be seen in Figure 3 (Deeke, 2015).

Separate charging and discharging has different advantages. When the granules are charged in the charging column, they are fluidized and can flow freely to achieve decent mixing and mass transfer of the substrate to the granules. When the granules are discharged, they are packed close together so that they can release the electrons and cations in a relatively small discharge cell, in which high currents can be achieved. The aim of the new Capacitive Moving Bed Reactor is to take the lessons learned from the fluidized bed reactor and improve the design.

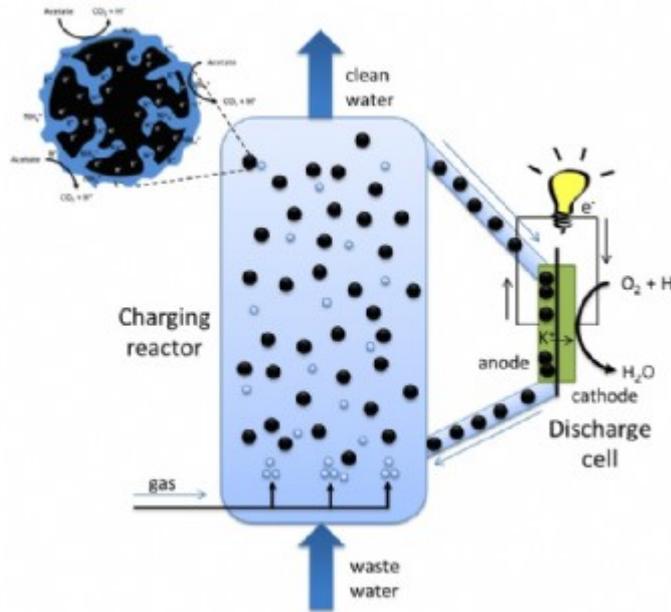


Figure 3 – Fluidized bed reactor by Deeke with charging column and discharging cell

Total Costs of the MFC

One of the key points to make the MFC more economically competitive is the reduction of the overall costs. At this moment the MFC is about 800 times more expensive than anaerobic systems (Rozendal 2008). Since the most expensive components of the MFC are the electrodes (anode and cathode) and the membrane, the greatest cost reduction for the material costs can be achieved if the costs of these components can be reduced. The activated carbon granules play an essential role in this part. As the conversion reactions take place in the biofilm on top of the granules that are fluidized in the charging column, the surface area of the anode in the discharge cell is not needed for the conversion reactions and can thus be reduced. So the size of the anode, cathode and membrane are reduced in the new Capacitive Moving Bed Microbial Fuel Cell compared to the rest of the reactor. Thus the costs are reduced by reducing the relative size of the anode, cathode and membrane compared to the total size of the reactor.

Scalability of the MFC

The final challenge that is addressed in the design of the new reactor, is the challenge regarding scalability of MFCs. The size of most MFCs is currently on lab scale with reactor volumes up to a few thousand millilitres (Janicek, 2014). Before the MFC can be applied to treat industrial or domestic wastewater, it has to be able to treat thousands of cubic meters of wastewater per day, with the same performance as reactors at lab scale. The bottleneck in scaling up an MFC is the close spacing of the anode, cathode and membrane.

The anode and membrane are currently spaced a few millimetres apart in most MFCs, in order to prevent voltage losses in the anolyte. The voltage loss in the anolyte (ΔE_s) is a function of the current density (I), the spacing between the anode and membrane (L) and the conductivity of the anolyte (σ_a) as described in Equation 3 (Rabaey, 2010).

$$\Delta E_s = I \cdot \frac{L}{\sigma_s} \quad (3)$$

To elaborate on this: if the voltage loss in the anolyte can maximally be 20% of the theoretical voltage limit, the maximal spacing of the anode and membrane can be calculated with the formula. Using a conductivity of 2500 $\mu\text{S}/\text{cm}$ for the wastewater (anolyte) and a current density of 10 A/m^2 , the maximal spacing between the anode and membrane can be 2.5 mm. So in order to increase the spacing between the anode and membrane, while preserving the same voltage loss, the conductivity of the anolyte has to be increased proportionately to the spacing of the anode and membrane. For the new reactor, the anolyte is assumed to be 25000 $\mu\text{S}/\text{cm}$, which is twenty-five times higher than ordinary wastewater with a low conductivity, that is 1000 $\mu\text{S}/\text{cm}$ (Taylor and Gardner 2007). This is because the activated carbon granules release a massive amount of the cations inside the discharge cell, which is assumed to create a locally high conductivity of the anolyte. If the conductivity is twenty-five times higher, the spacing between the anode and membrane can be twenty-five times higher to maintain the same voltage losses. However, actual research into the reactor and the conductivity of the anolyte in the discharge cell has to confirm if the conductivity is actually as high as is assumed. An overview of different types of water and the corresponding conductivities is made in Table 1 to increase the understanding in this topic (Liu et al. 2005; Rozendal et al. 2008; Taylor and Gardner 2007).

Table 1 - Approximate conductivity values of different types of water

Type of Water	Conductivity [$\mu\text{S}/\text{cm}$]
Tap Water	50 - 800
Domestic Wastewater – Low Conductivity	1000
Domestic Wastewater – High Conductivity	5000
Industrial Wastewater	10000
Anolyte in Discharge Cell of CMB-MFC	25000
Seawater	55000

Modelling the performance of the Capacitive Moving Bed MFC

Model Description

The overall performance of the capacitive moving bed reactor depends on many input variables. To gain an understanding between the relationships of the input variables and their effect on the performance of the reactor, a model has been made in Microsoft Excel. This model contains one part in which the input variables / design parameters are inserted and a second part in which the output that is calculated from these variables is displayed. The output part also contains additional tables and graphs to enhance the understanding of some specific design parameters. These tables and graphs are used to answer the subquestions of this thesis. For the input part the information about the granules (like density, weight and specific capacitance) and the information about the reactor (like dimensions and materials used in the discharge cell and the reactor) are inserted. The output part displays the areas of the components and the volume of the discharge cell, information about the resistances, current and power output, plus the tables and the corresponding graphs. A flow diagram is made to visualise the relations between the different inputs and outputs which is given in Figure 4 on page 10. The different blocks in the flow diagram show that the calculations are both done in parallel and successive steps. The required results for the analysis of the performance of the reactor are calculated in Step III, IV and V of the flow diagram.

Input Section

This section describes the input variables that are used in the model to compute the information for the output. First the dimensions of the discharge cell are inserted, based on the latest information about the design of the new reactor. The information regarding the electrical resistivity of the electrodes, membrane, anolyte and catholyte is inserted in the second part to compute the resistances of these parts. Thirdly the data of the activated carbon granules are inserted. The current production and capacitive behaviour of individual carbon granules was investigated in a recent study by Borsje, Liu and ter Heijne (Borsje, 2015). The data of two different activated carbon granules from this study is used to compute the relation between the type of granule that is used and the performance of the reactor. Finally some additional information about the volumes of the reactor is inserted and information about voltage losses at the anode and cathode, plus the maximum cell voltage are included. The individual input categories are elaborated in the following paragraphs.

Dimensions of Discharge Cell

The new capacitive moving bed reactor is designed as a tubular microbial fuel cell in which the electrodes and membrane in the discharge cell are configured in concentric tubes. The radii of these tubes (anode, cathode and membrane) are inserted in the model, which are later used to calculate the areas of these components and the volume of the discharge cell. For the new reactor these radii are 3.60 cm for the anode, 4.04 cm for the membrane and 4.70 cm for the cathode. The other data that is inserted are the height of the electrodes and membrane (which is 10 cm) and the width of the flowchannel (through which the granules flow to release the electrons and cations), which is designed to be 0.5 cm. The conductivity of the anolyte and catholyte are also inserted here, which are set to 25000 in $\mu\text{S}/\text{cm}$ for the anolyte and 20000 $\mu\text{S}/\text{cm}$. These values are later converted and expressed as electrical resistivity, so that they can be used to calculate the internal resistance. The design and dimensions of the discharge cell is illustrated in Figure 5 on page 11. The design of the entire reactor is illustrated in Figure 12 in the Appendix on page 29.

Input Section

Dimensions of Discharge Cell

- Radius Anode - r_a
- Radius Cathode - r_c
- Radius Membrane - r_m
- Height - h
- Flowchannel - f
- Conductivity Anolyte - σ_a
- Conductivity Catholyte - σ_c

Materials of Discharge Cell

- Elec. Resistivity Anode - ρ_a
- Elec. Resistivity Cathode - ρ_c
- Elec. Resistivity Membrane - ρ_m
- Elec. Resistivity Catholyte - ρ_{cath}
- Elec. Resistivity Anolyte - ρ_{ano}

Specifics of Carbon Granules

- Bulk Density - ρ_b
- Weight per Granule - m_g
- Volume per Granule - v_g
- Current per Granule - I_g
- Envelope Capacitance - C_e
- Bulk Capacitance - C_b
- Charge Time - t_c
- Discharge Time - t_d

Materials of Reactor

- Charging Column - V_{column}
- Discharge Cell - V_{cell}

Voltage Information

- Voltage Loss Anode - η_a
- Voltage Loss Cathode - η_c
- Maximum Cell Voltage - E^0
- Potential Anode – Granule - E_{An}

Output Section

Step I – Area, Volume & Flow Rate of Cell

- Total Area Anode - $A_{anode} = 2 \cdot \pi \cdot r_a \cdot h$
- Total Area Cathode - $A_{cathode} = 2 \cdot \pi \cdot r_c \cdot h$
- Total Area Membrane - $A_{mem} = 2 \cdot \pi \cdot r_m \cdot h$
- Volume Discharge Cell - $V_{cell} = (\pi \cdot r_m^2 - \pi \cdot r_a^2) \cdot h$
- Total Volume - $V_{tot} = V_{cell} + V_{column}$
- Flowrate - $Q_{cell} = V_{cell} / t_d$

Step II – Resistances of Components in Cell

- Resistance Anode - $R_a = \rho_a \cdot (l / A_{anode})$
- Resistance Cathode - $R_c = \rho_c \cdot (l / A_{cathode})$
- Resistance Membrane - $R_m = \rho_m \cdot (l / A_m)$
- Resistance Catholyte - $R_{cath} = \rho_{cath} \cdot (l / A_{cathode})$
- Resistance Anolyte - $R_{ano} = \rho_{ano} \cdot (l / A_{anode})$
- Total Resistance - $R_{tot} = \text{SUM} \wedge \wedge \wedge$

Step III – Current Information

- Volumetric Current Density - $I_{vol} = (\rho_b \cdot I_g) / m_g$
- Current via Current Density - $I_p = I_{vol} \cdot V_{cell}$
- Current via Bulk Capacitance - $I_{bulk} = (V_{cell} / t_d) \cdot C_b \cdot E_{An}$

Step IV – Power Information

- Cell Voltage - $E_{cell} = E^0 - \eta_a - \eta_c - I \cdot R_{tot}$
- Power - $P = E_{cell} \cdot I$
- Power Density - $P_v = P / V_{tot}$

Step V - Additional Tables and Graphs

- Variation of Current - I vs. P_v
- Variation of Analytic Conductivity - σ_a vs. P_v
- Variation of Discharge Time - t_d vs. P_v
- Variation of Width Flowchannel - f vs. P_v

Figure 4 – Flowdiagram of the calculations in the Model

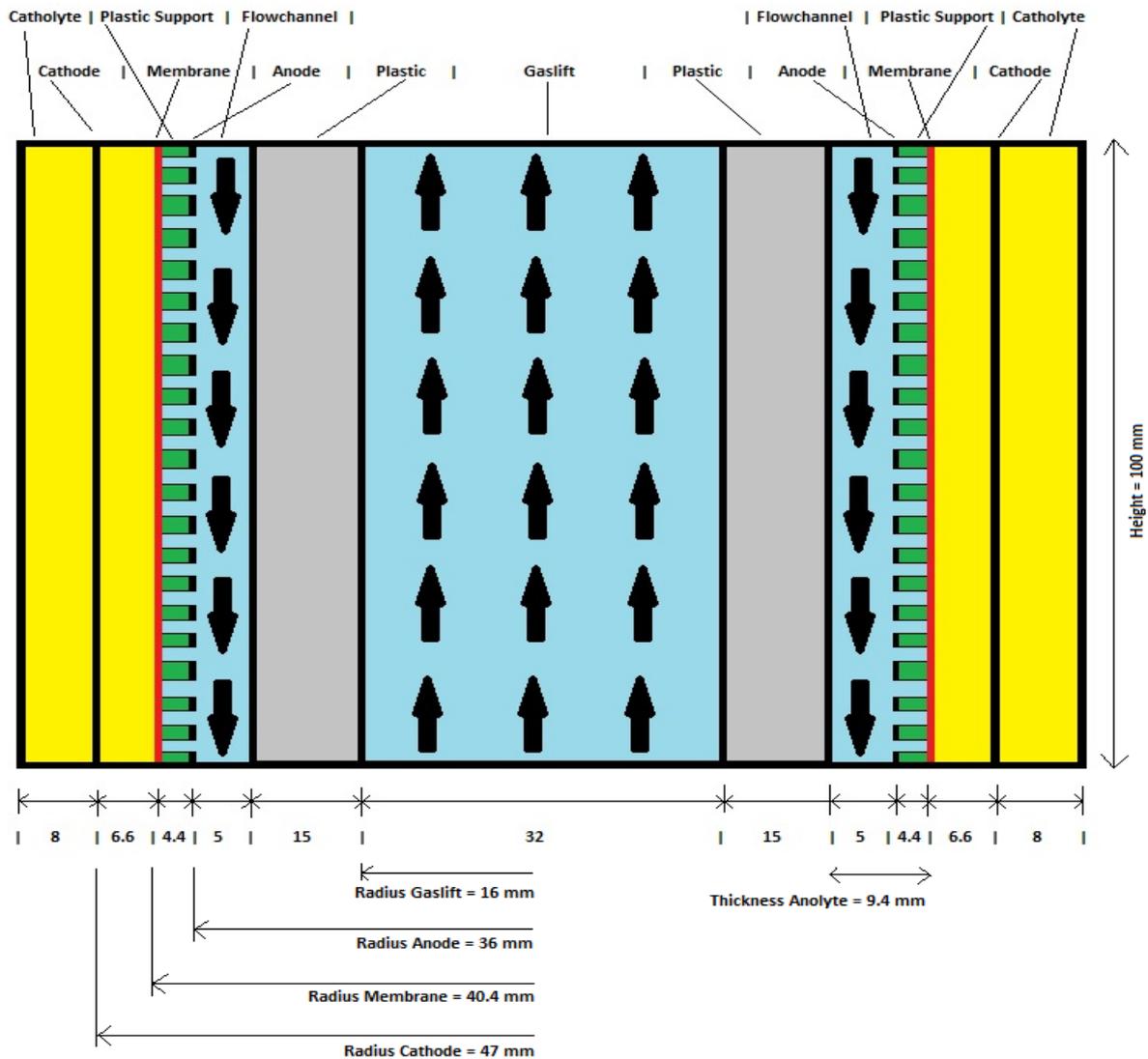


Figure 5 - Design and Dimensions of the Discharge Cell

Materials of Discharge Cell

In this section the electrical resistivity ($\Omega \cdot \text{cm}$) and thickness (cm) of the different components in the discharge cell are inserted. These components are the anode, cathode, membrane, anolyte and catholyte. This information is used to calculate the resistances for each of these components, which are added together with the idea that they behave as multiple resistors in series, to compute the total internal resistance (Ω). The materials should have a very low electrical resistivity to minimize the total internal resistance. Therefore platinum coated magneto mesh is selected for the electrodes, which has an electrical resistivity of $1.06 \cdot 10^{-5} \Omega \cdot \text{cm}$ and a Fumasep FKE membrane is selected for the membrane that has an electrical resistivity of $3 \Omega \cdot \text{cm}$ (Fumasep FKE, FuMA-Tech GmbH, St. Ingbert, Germany). The anolyte consists of the wastewater, which is assumed to have locally high conductivity inside the discharge cell of $25000 \mu\text{S}/\text{cm}$ or $40 \Omega \cdot \text{cm}$ when expressed as electrical resistivity. The anolyte consists of ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$), which as an conductivity of $20000 \mu\text{S}/\text{cm}$ or $50 \Omega \cdot \text{cm}$ when expressed as electrical resistivity. The prices of the components are also inserted in this section, which are added together so that the overall price of the discharge cell the reactor can later be calculated.

Specifics of Carbon Granules

The two type of activated carbon granules that are used in the reactor are the PK 1-3 granule and the GAC 1240 granule, both from Cabot Norit, hereafter denoted as PK and GAC granule, (Granular Activated Carbon, Cabot Corp, Amersfoort, The Netherlands). These specific granules are selected since they demonstrated a promising capacitive performance in the study by Borsje et al. (envelope capacitance: 72.6 F/cm³ for the PK granule and 18.6 F/cm³ for the GAC granule). For each granule the bulk density (0.24 g/cm³ for the PK granule and 0.51 g/cm³ for the GAC granule), the weight (10.2 mg for the PK granule and 6.6 mg for the GAC granule) and volume ($9.9 \cdot 10^{-3}$ cm³ for the PK granule and $6.2 \cdot 10^{-3}$ cm³ for the GAC granule) are inserted. The envelope and bulk capacitance per granule (F/cm³), current per granule (0.59 mA for the PK granule and 0.16 mA for the GAC granule) and charge- plus discharge time are also inserted (s), based on the study by Borsje et al (Borsje, 2015). The discharge times of the granules are both set at 180 seconds, based on the fixed potential experiments by Borsje et al. The information of the granules is used to calculate the current (density) in various ways.

Materials of Reactor

This section is used to calculate the volumes of the components of the reactor, which are added together to calculate the total volume of the reactor, which is used to calculate the volumetric power density of the reactor (with a height of 60 cm and diameter of 11 cm, the charging column is 5.2 L). The remaining prices of the other reactor components can also be inserted here.

Voltage Information

In this part additional information is inserted that is needed to calculate the cell voltage. These are the voltage losses at the anode and cathode (both 0.2 V), plus the maximum cell voltage (1.09 V). The potential between the anode and the granule (0.2 V) is also inserted here, which is used to calculate the current of the reactor.

Output Section

This section describes how the input data is used to calculate the various quantities in the output section. The equations for these calculations are included to gain a thorough understanding in the subject matter. First the area of the components in the discharge cell and the volume of the cell are calculated, secondly the resistances of the components within the discharge cell are computed, than the current and finally the power and power densities are calculated, as described below.

Area, Volume and Flowrate of Discharge Cell

The data of the radii and the height of the components in the discharge cell is used to calculate the area of these components. The information about these areas is needed to calculate the electrical resistances of these components and the areal current density of the discharge cell. The calculation for the area is given with Equation 4, in which (A) is the area of the component (anode, cathode or membrane), the radius at which the components is located from the centre of the reactor is given with (r) and the height of the component is given with (h).

$$A = 2 \cdot \pi \cdot r \cdot h \quad (cm^2) \quad (4)$$

The same data (radii and height) is used to calculate the volume of the discharge cell (or the volume of the flowchannel). The information about the cell volume is later needed to calculate the current and the flowrate through the discharge cell. The calculation for the volume is given with Equation 5, in which (V_{cell}) is the volume of the discharge cell, (r_a) is the radius of the the anode, (f) is the width of the flowchannel and (h) is the height.

$$V_{cell} = (\pi \cdot r_a^2 - \pi \cdot (r_a - f)^2) \cdot h \quad (mL) \quad (5)$$

The total volume of the reactor (V_{tot}) is the combination of the volume of the discharge cell (V_{cell}) and the charging column (V_{column}), as given in Equation 6.

$$V_{tot} = V_{cell} + V_{column} \quad (mL) \quad (6)$$

Another important value is the flowrate of the carbon granules through the discharge cell. The volume of the discharge cell (V_{cell}) and the discharge time of the granules in the cell (t_d) are used to calculate the flowrate (Q_{cell}), as given in Equation 7.

$$Q_{cell} = V_{cell} / t_d \quad (mL/s) \quad (7)$$

Resistances of Components in Discharge Cell

The information of the electrical resistivity and thickness of the components in the discharge cell is used to compute the resistance of each of these components. However, the conductivity of the anolyte and catholyte is first converted to electrical resistivity with Equation 8.

$$\rho_{el} = 1 / (\sigma \cdot 10^{-6}) \quad (\Omega \cdot cm) \quad (8)$$

With the electrical resistivity of all the components, the resistance (R) of the component is calculated by multiplying the electrical resistivity (ρ_{el}) with thickness of the component (l), which is divided by the area (A) of the component that was calculated earlier, as given in Equation 9. The resistance of each component is added together to get one value for the total internal resistance of the discharge cell.

$$R = \rho_{el} \cdot (l / A) \quad (\Omega) \quad (9)$$

Current Information

Various methods are used to calculate the current. For the first method a value is taken in which the carbon granule produces current in continuous mode. This is 0.59 mA for the PK granule (with a weight of 10.2 mg and bulk density of 0.24 g/cm³) and 0.16 mA for the GAC granule (with a weight of 6.6 mg and bulk density of 0.51 g/cm³). These values are used to calculate the volumetric current density and then multiplied by the volume of the discharge cell to compute the current. The overall calculation is given in Equation 10, with the current as (I), the bulk density as (ρ_b), the current produced by the single granule as (I_g), the weight of the granule as (m_g) and the volume of the discharge cell as (V_{cell}).

$$I = ((\rho_b \cdot I_g) / m_g) \cdot V_{cell} \quad (A) \quad (10)$$

For the second method to calculate the current (I), the capacitive behaviour of the carbon granule is taken into account and therefore the bulk capacitance of the granule (C_b) is used, which is 16.9 F/cm³ for the PK granule and 8.9 F/cm³ for the GAC granule. The discharge time of the granule (t_b) is also used in this calculation, as is a value for the potential between the anode and the granule (E_{An}), which is given in Equation 11.

$$I = (V_{cell} / t_d) \cdot C_b \cdot E_{An} \quad (A) \quad (11)$$

The Solver function of Excel is used to compute the current at which the highest power density is generated. The Solver function in Excel maximises the value in the cell that displays the power density by changing the number in cell in which the current is inserted, as can be seen in Figure 6.

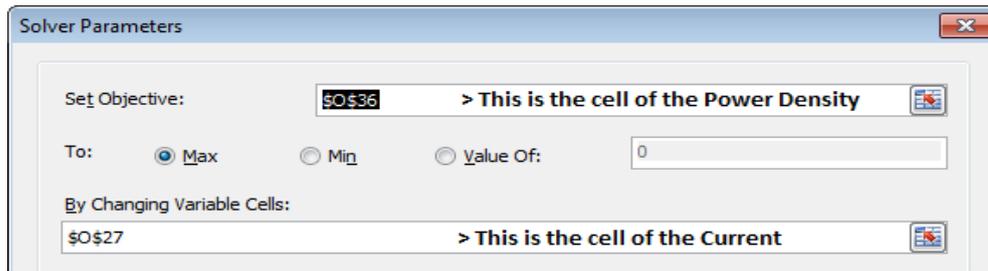


Figure 6 - The Solver Function in the Model

Power Information

With the value for the current, the power of the reactor can be calculated. However, the cell voltage has to be calculated first, which is done by subtracting the voltage losses from the maximal theoretical cell voltage, as was described in equation 2. The maximum theoretical cell voltage (E^0) is taken to be 1.09 V, the voltage losses at the electrodes (η_a) and (η_c), are estimated at 0.2 V each. To calculate the losses due to internal resistance, the previously calculated current (I) is multiplied by the previously calculated total internal resistance (R), as given in Equation 2.

$$E_{cell} = E^0 - \eta_a - \eta_c - I \cdot R \quad (V) \quad (2)$$

The power output of the reactor (P) can then be calculated by multiplying the cell voltage (E_{cell}) with the current (I) as is given in Equation 12.

$$P = E_{cell} \cdot I \quad (W) \quad (12)$$

The volumetric power density of the reactor (P_a or P_v) can subsequently be calculated by dividing the power (P) by the anode surface area (A_{anode}) or by the total volume of the reactor (V_{tot}), or by the volume of the discharge cell (V_{cell}), depending on the preferred choice, as given in Equation 13 and 14.

$$P_a = P / A_{anode} \quad (W/m^2) \quad (13)$$

$$P_v = P / V_{tot} \quad (W/m^3) \quad (14)$$

Additional Tables and Graphs

To answer the subquestions, extra insight is needed to understand how some design parameters affect the performance of the reactor (in terms of volumetric power density output). Therefore additional tables and graphs are made that investigate these design parameters. The design parameter is varied (the independent variable on the x-axis) and the same steps are taken to calculate the power density output (the dependent variable on the y-axis) as described in previous parts. In this way the effect that the specific design parameter has on the performance of the reactor becomes clear. The design parameters that are investigated are the current, the conductivity of the anolyte, the discharge time of the granules in the discharge cell and the width of the flowchannel.

Research Results

Volumes and Flowrate Information

With the given dimensions for the components, the area of the anode is 226.20 cm², the volume of the discharge cell is 105.61 mL or $1.05 \cdot 10^{-4}$ m³ and the total volume of the reactor is 5.33 L or $5.33 \cdot 10^{-3}$ m³. When the discharge time is set at 180 seconds, the flowrate of the granules through the discharge cell will be 0.58 mL/s, or 35.1 mL/min .

Resistance Information

The selection for the electrodes and membrane of the CMB-MFC is based on electrical resistivity of the materials. The value for the resistances are calculated to be $4.69 \cdot 10^{-9}$ Ω for the anode and $3.59 \cdot 10^{-9}$ Ω for the cathode. The membrane has an estimated resistance of $7.09 \cdot 10^{-5}$ Ω. So the resistance of these components are very low. However there also additional losses at the electrodes, which are expressed in the overpotential losses for the anode and cathode. When these potential losses are converted to resistance values, these are 0.16 Ω for each electrode. The resistance of the anolyte and catholyte are estimated 0.17 Ω for the anolyte and 0.11 Ω for the catholyte. For this situation the conductivity of the anolyte is assumed to be 25000 μS/cm (due to the locally high conductivity in the discharge cell), which is twenty-five times higher than ordinary wastewater that is 1000 μS/cm (Taylor and Gardner 2007). The total resistance is calculated to be 0.278 Ω, or 0.600 Ω when the overpotential losses are added into this resistance equation.. The distribution of each component to the internal resistance is displayed in the pie chart of Figure 7, which includes the overpotential losses.

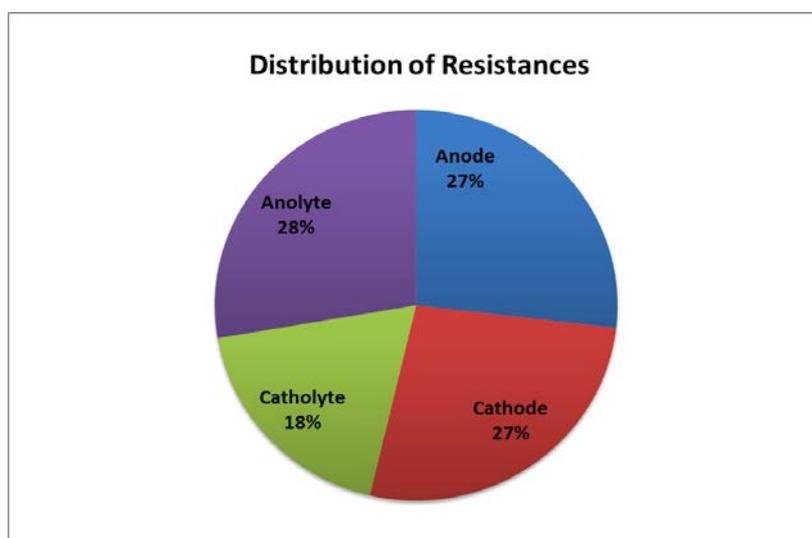


Figure 7 – Distribution of Resistances

Current Information

Different methods are used to calculate the current from the discharge cell. When the calculation is used in which the carbon granules are assumed to produce current in continuous mode, the current is 1.47 A for the PK granule and 1.31 A for the GAC granule. With the calculation that includes the capacitive behaviour of the granule and a discharge time of 180 seconds for each granule, the current is estimated to be 1.98 A for the PK and 1.05 A for the GAC granule. According to the calculations by the Solver, the current which produces a maximum power density is estimated to be 1.24 A.

When these values are expressed in areal current density (the current divided over the area of the anode), the values are 64.82 A/m² for the PK granule and 57.72 A/m² for the GAC granule in continuous mode. For the capacitive method the areal current densities are 87.73 A/m² for the PK granule and 46.23 A/m² for the GAC granule. For the situation in which the current is optimal, the areal current density is 54.86 A/m².

The current values can also be expressed in volumetric current density (the current divided over the total volume of the reactor). In this way the values are 275.32 A/m³ for the PK granule and 245.20 A/m³ for the GAC granule in continuous mode. For the capacitive method the volumetric current densities are 372.66 A/m³ for the PK granule and 196.36 A/m³ for the GAC granule. For the situation with an optimal current, the volumetric current density is 233.01 A/m³. All these different values are displayed in Table 2.

Table 2 - Values for Current, Areal Current Density and Volumetric Current Density

Quantity	Unit	Optimal	PK Granule		GAC Granule	
			Continuous	Capacitive	Continuous	Capacitive
Absolute Current	[A]	1.24	1.47	1.98	1.31	1.05
Current Density	[A/m ²]	54.86	64.82	87.73	57.72	46.23
Current Density	[A/m ³]	233.01	275.32	372.66	245.20	196.36

Power Information

When the current is optimal at 1.24 A, the voltage loss is 0.75 V and the cell voltage is 0.34 V. In this situation the reactor will generate a power of 0.43 W and has a volumetric power density of 18.93 W/m² or 80.39 W/m³. With a generated current of 1.47 A by the PK granule in continuous mode, the voltage loss is 0.81 V, the cell voltage of 0.28 V, the power is 0.41 W and the power density is 18.33 W/m² or 77.74 W/m³. If the current value for the PK granule in capacitive mode is taken, the voltage loss is 0.95 V, the cell voltage of 0.14 V, the power is 0.27 W and the power density is 12.25 W/m² or 51.51 W/m³. When the same calculations are done for the GAC granule in continuous mode, the voltage loss is 0.76 V, the cell voltage is 0.33 V, the power is 0.43 W and the power density is 18.88 W/m² or 80.17 W/m³. For the capacitive mode the voltage loss is 0.69 V, the cell voltage is 0.40 V, the power is 0.42 W and the power density is 18.44 W/m² or 78.4 W/m³. All these different values are displayed in Table 3.

Table 3 - Values for Voltage Loss, Cell Voltage, Power and Power Density

Quantity	Units	Optimal	PK Granule		GAC Granule	
			Continuous	Capacitive	Continuous	Capacitive
Voltage Loss	[V]	0.75	0.81	0.95	0.76	0.69
Cell Voltage	[V]	0.34	0.28	0.14	0.33	0.40
Absolute Power	[W]	0.43	0.41	0.27	0.43	0.42
Power Density	[W/m ²]	18.93	18.33	12.25	18.88	18.44
Power Density	[W/m ³]	80.39	77.74	51.51	80.17	78.40

The calculated values of the current and corresponding power density of the PK and GAC granule (both for continuous and capacitive mode) are very close to the current value that generates the highest power density, as can be seen in Table 2 and 3.

Comparison of Microbial Fuel Cells

The results from the calculations are compared with similar reactor systems to interpret the calculated values and investigate how well the CMB-MFC performs. The MFC's that are selected for this comparison have a reactor volume on the litre scale and use carbon granules for the production of the current (either granular graphite or activated carbon). The systems are operated in continuous mode (the carbon granules continuously supply the anode with electrons in one location) or in intermittent mode (the carbon granules are first charged in one location and then discharged at another location). The selected systems for this comparison are the upflow microbial fuel cell (UMFC) by Zhang et al. (Zhang, 2010), the fluidized bed membrane bioelectrochemical reactor by Li et al. (Li, 2014) and the fluidized capacitive bioanode by Deeke et al. (Deeke, 2015). The results of these studies combined with the results from the calculations of the model in this thesis can be seen in Table 4.

The outcome from the current information of the granules in capacitive mode is selected for the input of the current and corresponding power information of this study. An additional quantity that is added in this table is the electrode density (m^2/m^3). The electrode density expresses the area of the electrodes over the total volume of the reactor to see how much space the electrodes occupy compared to the rest of the reactor. Since the absolute current and absolute power of the other systems have low values, these quantities are expressed in (mA) and (mW).

Table 4 - Comparison of Different L-scale MFC

Quantity	Units	Zhang	Li	Deeke	This Study	This Study
Type Reactor	[-]	TCT-BP ^a	FB-ISD ^b	FB-ED ^c	FB-ED*	FB-ED*
Operation Style	[-]	Continuous	Continuous	Intermittent	Intermittent	Intermittent
Granule Type	[-]	GG ^d	GAC 830	GAC 830	GAC 1240	PK 1-3
Electrode Area	[cm ²]	4899	706	11	226	226
Electrode Density	[m ² /m ³]	99.98	79.86	0.52	4.24	4.24
Volume Dis.-Cell	[mL]	nvt	nvt	22	105	105
Volume Total	[mL]	4900	884	2102	5325	5325
Flowrate	[mL/min]	300	800	500	35.1	35.1
Internal Resistance	[Ω]	7.02	56.52	???	0.278	0.278
Absolute Current	[mA]	161.7	11.5	1.43	1050	1980
Current Density	[A/m ²]	0.33	0.16	1.3	46.1	87.4
Current Density	[A/m ³]	33	8	0.69	195.7	371.4
Absolute Power	[mW]	76	1.26	???	420	270
Power Density	[W/m ²]	0.15	0.017	???	18.44	12.25
Power Density	[W/m ³]	15.52	1.8	???	78.33	51.51

^aTCT-BP: Two chamber, packed bed

^bFB-ISD: Fluidized bed, in situ discharge

^cFB-ED: Fluidized bed, external discharge

^dGG: Granular graphite with particle size distribution of 10 mm

Compared to the other reactors, the CMB-MFC performs significantly better in terms of absolute current, current density, power and power density. This is probably due to low internal resistance, which is caused by the high conductivity in the discharge cell and the close spacing of electrodes and membrane. However, this close spacing of the electrodes and membrane and the slow movement of the carbon granules through the discharge cell, causes a flowrate that is one order of magnitude lower than the other reactors.

Investigation of Input Variables

Some input variables and design parameters are further investigated to study the effect of these variables on the performance of the reactor in terms of power density. This information is used to answer the subquestions and can also be used to improve the design of the reactor.

Power Curves

The first parameter that is investigated for its effect on the power density, is the current. A table is made in which the current varies from 0.0 to 3.0 A in steps of 0.2 A. For each value of the current, the corresponding voltage loss, cell voltage, power and power density is calculated. The power density is displayed as a function of the current in which the corresponding curves are known as power curves, as can be seen in Figure 8. These calculations are made for four different values of the anolytic conductivity to see how the anolytic conductivity and thus the internal resistance affects the power density. The figure shows that when the anolytic conductivity increases, the internal resistance decreases and therefore the maximum attainable power increases. The current value at which these maximum power can be achieved, increases as well. So the maximum power output depends on the internal resistance of the reactor, which depends on the input variables like anolytic and catholytic conductivity, resistance of the electrons and membrane, width of the flowchannel, etc. So the smaller the internal resistance, the higher the maximal power output that can be achieved.

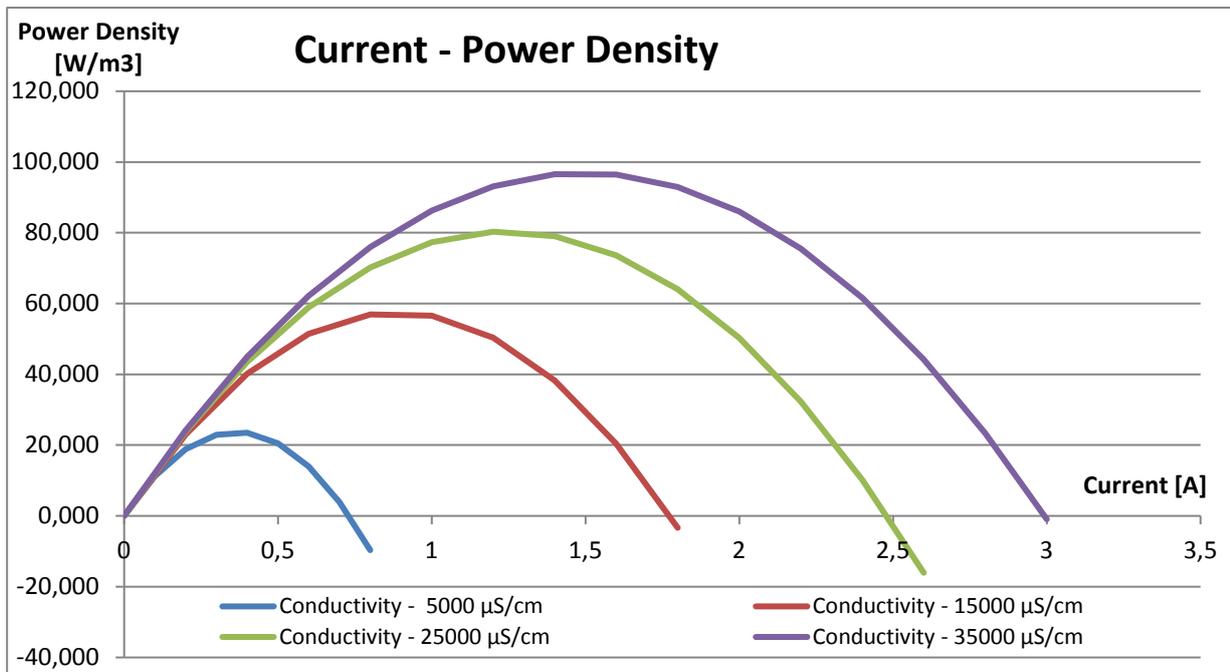


Figure 8 – Current vs. Power Density

Anolytic Conductivity

The second parameter that is studied for its relation with the power density, is the conductivity of the anolyte. For this parameter a table is made in which the conductivity varies from 2500 to 50000 $\mu\text{S}/\text{cm}$, in steps of 2500 $\mu\text{S}/\text{cm}$. Each value of the conductivity is first converted to electrical resistivity ($\Omega \cdot \text{cm}$) and then multiplied by the total thickness of the anolyte to get the areal resistivity ($\Omega \cdot \text{cm}^2$). The areal resistivity is subsequently divided by the area of the anode to get a value for the resistance of the anolyte (Ω). This resistance is added to the values of the resistance of the other components in the discharge cell to get a value for the total internal resistance. This number is used to calculate the voltage loss, cell voltage, power and finally power density in the same way as described earlier in the thesis.

These calculations are made for three different current values (of 0.6, 1.2 and 1.8 A) to get a thorough understanding of the effect of the current value in relation to the conductivity of the anolyte.

The table and the corresponding graph in Figure 9 show that the power density is negative for low values of the anolytic conductivity and rises with incrementally smaller steps. By investigating the anolytic conductivity for three different current values, it becomes clear that the current of 0.6 A generates the highest power density up to 15000 $\mu\text{S}/\text{cm}$, followed by the current of 1.2 A that generates the highest power density between 1500 $\mu\text{S}/\text{cm}$ up to 37500 $\mu\text{S}/\text{cm}$, after which it is taken over by the current of 1.8 A which generates the highest power densities for 37500 $\mu\text{S}/\text{cm}$ and higher.

Figure 9 is similar to Figure 8, with the difference that the current is on the x-axis in Figure 8 and the conductivity is on the x-axis in Figure 9. The conclusion on the performance is therefore the same: the maximum attainable power for a specific conductivity depends on the current, while the maximum attainable power for a specific current is generated by the highest conductivity.

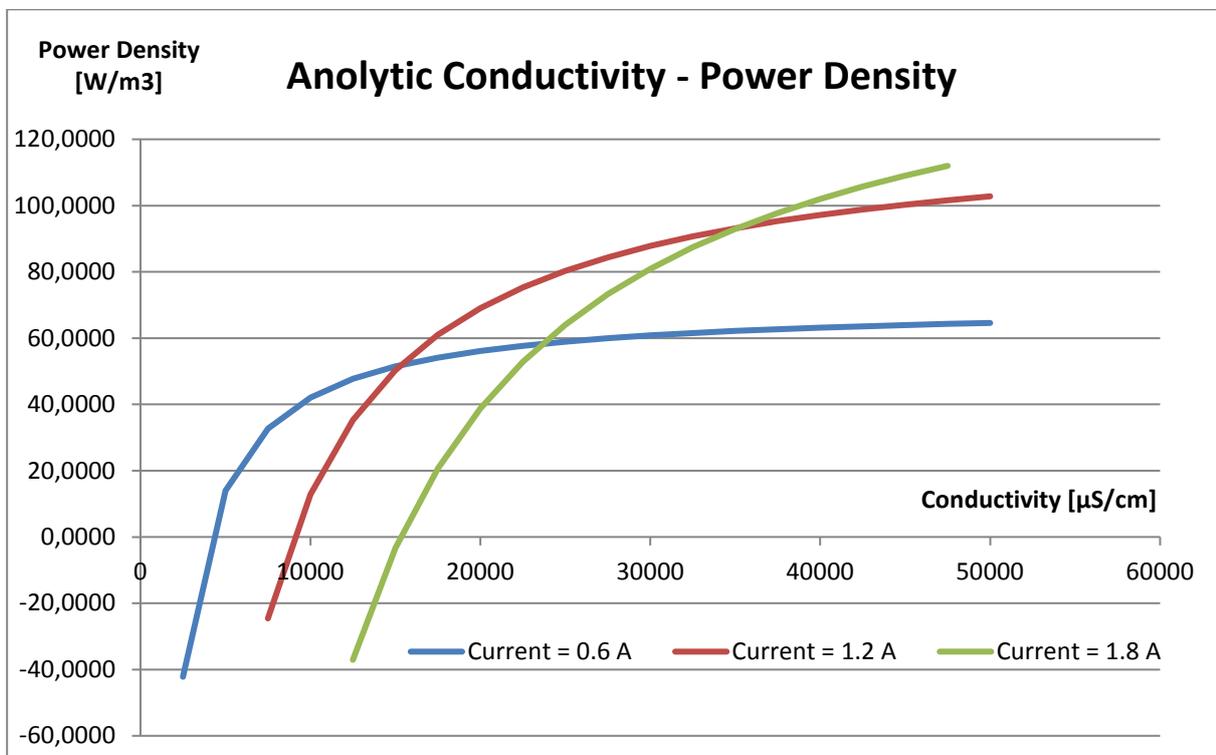


Figure 9 – Analytic Conductivity vs. Power Density

Discharge Time

The third parameter that is investigated for its relation to the power density, is the discharge time. To investigate this parameter, actual measurements are taken from the study by Borsje et al. In this study an individual activated carbon granule (the PK and GAC granule) was charged and discharged from 0 to 180 seconds at a fixed potential of 0.3 V. The current that was produced by the individual granule was logged from 0 to 180 seconds in steps of 0.1 seconds. These current values from individual granules are converted to a current value from the discharge cell with the assumption that the volume of the discharge cell is filled with these granules (using the information about the bulk density and weight of the granule and the volume of the discharge cell). This current value from the discharge cell is used to calculate the corresponding voltage loss, cell voltage, power and power density of the reactor, in the same way as described previously.

The table and corresponding graph in Figure 10 show that the power density is negative till about 10.5 seconds for the PK granule and till about 30.9 seconds for the GAC granule. The reason for this is the high current output from the granules in the first seconds of discharge. When the current output of the granules is so high (4.6 A for the PK and 6.6 A for GAC granule at 0.1 s of the discharge), the voltage losses become too large, and therefore the eventual power output is negative. The power density rises to a maximum of 72 W/m³ for the PK granule and 37 W/m³ for the GAC granule (power output divided by the total volume of the reactor). The power density reaches the proximity of this maximum power density after about 70 seconds, as can be seen in Figure 10. The power output from the PK and GAC granule with a current output in continuous mode is added in this figure for a comparison. The values for this are 77.7 W/m³ for the PK granule and 80.2 W/m³ for the GAC granule as was calculated earlier.

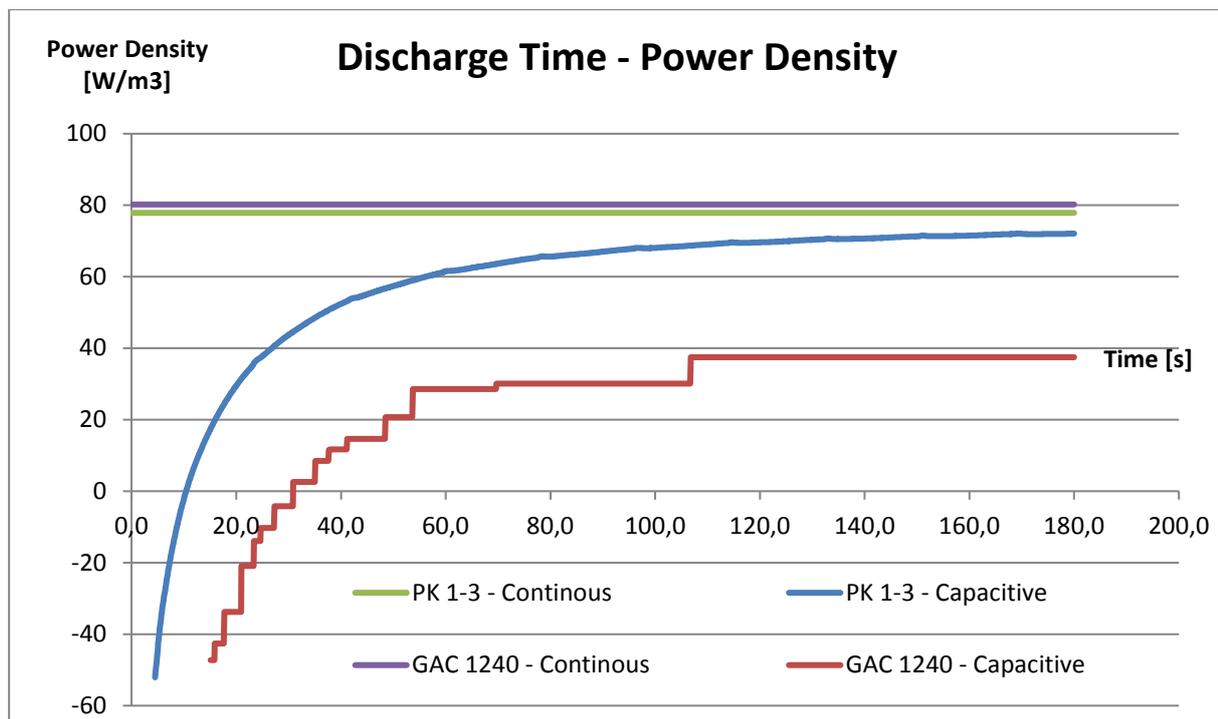


Figure 10 – Discharge time vs. Power Density of PK and GAC granule

Flowchannel

The final parameter that is investigated for its relation to the power density, is the width of the flowchannel (the space between the anode and the plastic tube, through which the carbon granules flow to release the electrons and cations to the electrodes, as can be seen in Figure 5). A table is made in which the width of the flowchannel varies from 0 to 2 cm, in steps of 0.1 cm. The value for the width is used to calculate the corresponding volume of the discharge cell (which is the volume of the flowchannel) and also the resistance caused by the anolyte in the discharge cell. For this calculation an anolytic conductivity of 25000 μS/cm is assumed. This information is used to calculate the current, total internal resistance, voltage loss, cell voltage, power and power density in the same way as the other calculations in the model.

These calculations are made for four different current values (PK granule in continuous and capacitive mode, and the GAC granule in continuous and capacitive mode) to see how the width of the flowchannel affects the performance of the selected granules and current methods.

The table and the corresponding graph in Figure 11 show that the granules perform differently depending on the width of the flowchannel. For example, the PK granule in capacitive mode has the highest performance at a width of 0.3 cm, while the GAC granule in capacitive mode has the highest performance at 0.5 cm. The range of the width of the flowchannel goes to a maximum of 1.0 cm, since all the values for the power density become negative after 1.0 cm, due to the large internal resistance caused in the anolyte of the flowchannel.

Another quantity that is calculated by varying the width of the flowchannel, is the flowrate (mL/min). The flowrate is expressed as a function of the width of the flowchannel in the graph of Figure 11. Since the values for the power density and the flowrate are in the same order of magnitude, the values on the y-axis can be used to read either the power density or the flowrate.

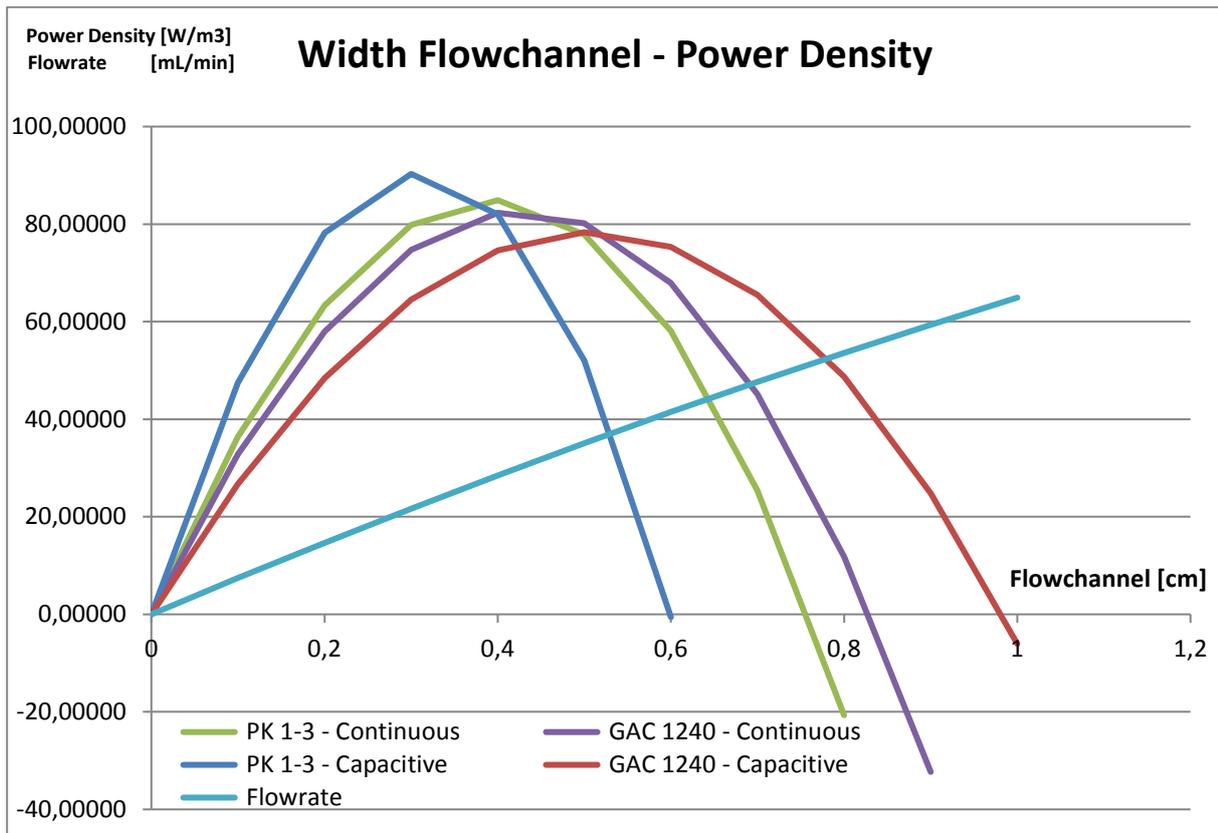


Figure 11 – Width Flowchannel vs. Power Density

Conclusion

The results from the calculations show that a higher power output can indeed be reached with the CMB-MFC. The first improvement of the reactor is the total internal resistance. With a calculated value of 0.278Ω , the new reactor has a total internal resistance that is more than one order of magnitude lower if compared with other reactors (that have internal resistances ranging from 7 to 57Ω). This is caused by the high conductivity of the anolyte and catholyte, the two parts that contribute for more than 99% of the total internal resistance. The second improvement is the current and current density of the reactor. With 46.1 A/m^2 for the GAC granule and 87.4 A/m^2 for the PK granule, the absolute current and current density that is released by the carbon granules is more than one order of magnitude larger than the current densities reached by the other reactors. The combination of a low internal resistance and high values for the current generate a high absolute power and power density, of which the (areal) power densities of 18.4 W/m^2 for the GAC and 12.3 W/m^2 for the PK granule are the highest calculated (areal) power density values in a MFC to date. The only part in which the new reactor performs worse compared to other reactors, is the flowrate of the granules through the discharge cell of reactor. The flowrate of 35.1 mL/min is one order of magnitude lower than similar reactors, which have flowrates of 300 to 800 mL/min . This low flowrate is caused by the small width of the flowchannel and slow movement of the granules through the discharge cell.

The additional research into the design parameters and input values of the reactor show that the maximum attainable power (density) output with the given design parameters is 80.4 W/m^3 , which is reached at a current of 1.24 A. The estimated current output (in capacitive mode) from the PK (2.0 A) and GAC (1.1 A) granule are relatively close to this value. The maximum attainable power depends on the internal resistance, which is a function of anolytic and catholytic conductivity, electrical resistivity of the electrodes & membrane and the width of the flowchannel. This maximum attainable power becomes larger if the internal resistance decreases.

Research into the anolytic conductivity shows that the maximal attainable power for a specific conductivity depends on the current output of the reactor: low current values generate the highest power output when the conductivity is low, while high current values produce the highest power when the conductivity is high. The higher the conductivity, the higher the power output can be.

The calculation methods for the discharge time show that the power output is negative during the first seconds of the discharge, which is caused by the high current output during this first seconds of the discharge. The power output rises with incremental smaller steps when the discharge time is higher.

When the maximal attainable power is estimated as a function of the flowchannel, the power output depends on the granule that flows through the flowchannel and the calculation method to calculate the current: the PK granule has the highest power output at a flowchannel width of 0.3 cm, while the GAC granule produces the highest power output at a width of 0.5 cm. The flowrate increases linearly when it is expressed as a function of the width of the flowchannel. The results of the research into the reactor can be used for the optimization of the new reactor.

Discussion

The results from the calculations of the model show that the CMB-MFC has a performance that is much higher than similar reactor systems. Therefore the CMF-MFC appears to be a promising new step in the development of MFC. However, the calculated performance depends on many input variables, of which some values are not completely clear. One example is the value that is used for the anolytic conductivity, which is estimated to be 25000 $\mu\text{S}/\text{cm}$. This value is twenty-five times higher than ordinary wastewater and half the conductivity of sea water. If the anolytic conductivity is indeed 25000 $\mu\text{S}/\text{cm}$ (or higher), this is a huge improvement in the development of MFCs, as it decreases the internal resistance and thereby increases the power output. If this value eventually turns out to be in the range of 1000 – 10000 $\mu\text{S}/\text{cm}$, the power output will probably be negative (if the other input variables stay the same). As the value of these input variables make such a huge difference, it is important to know exactly what these values are.

Since the strength of the anolytic conductivity depends on the amount of cations in the water, it is likely that a high current causes a high anolytic conductivity because the carbon granules that release a high amount of electrons (that generate a high current in the load), are assumed to also release a high amount of cations (that contribute to a high value for the conductivity).

Another uncertainty is how the discharge time affects the performance of the reactor. For the discharge calculations in the model, the current data from the individual granules at a fixed potential (by Borsje et al.) are converted to a current and power output from the reactor. These calculations show that the high currents during the first seconds of the discharge cause high voltage losses and therefore negative power values. However, it might be the case that these high currents produce a high anolytic conductivity (as was described in the previous paragraph) and therefore the power might not be negative as is currently calculated. Another uncertainty is in the discharge volume that is used for these calculations: when the current is calculated, the entire volume of the discharge cell is used in the calculation. If only one tenth of the volume of the discharge cell is used (which assumes that the high current occurs only locally in the discharge cell), the current becomes ten times smaller, which produces a power output that is positive. Real life experiments can demonstrate how the reactor performs with different discharge times.

Recommendations

With the knowledge gained after modelling the CMB-MFC, recommendations are given to improve the design of the reactor. The design improvements are given with the aim to increase the performance of the reactor, or decrease the total costs of the reactor.

At this moment the electrodes and membrane have a contribution of 0.03% to the total internal resistance. Since these are the most expensive components of the reactor, the construction costs can be decreased if cheaper electrodes and membrane are used, while maintaining the low resistances of these components. If the thickness of these components remain the same, the electrical resistivity of the electrodes can be increased from $1.06^{-5} \Omega\cdot\text{cm}$ to $10.6 \Omega\cdot\text{cm}$ and the electrical resistivity of the membrane from $3 \Omega\cdot\text{cm}$ to $300 \Omega\cdot\text{cm}$. This will increase their contribution to only 5.24% of the total internal resistance.

The value for the strength of the conductivity inside the discharge cell is not clear. Since this factor has a strong contribution to the power output, it is advised to do test on the actual strength of the conductivity inside the discharge cell and see if the conductivity increases with higher currents (and thus cations?).

Between the membrane and the anode is a plastic support that contributes to 28 % of the total internal resistance. If this plastic support can be removed (leaving only the anode, flowchannel and membrane), the power density will increase by 38 %.

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Appendix

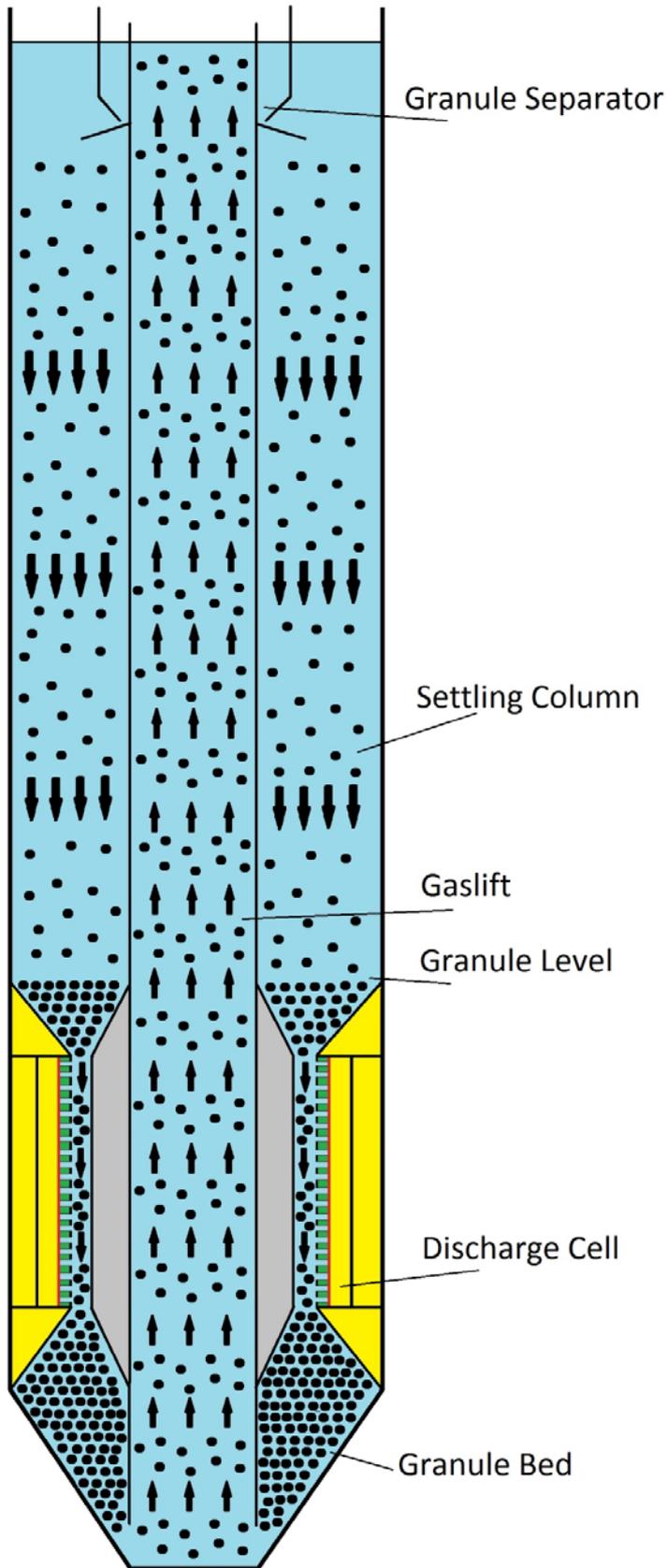


Figure 12 - Design of the Capacitive Moving Bed Reactor