Improving bio-electricity production and waste stabilization in Microbial Fuel Cells

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PhD Thesis

A submission presented in partial fulfillment of the requirements of the University of South Wales/Prifysgol De Cymru for the degree of Doctor of Philosophy
Dedication

To my parents

Für meine Eltern (Hans and Roswitha Fradler)
Acknowledgement

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Abstract

Biological wastewater treatment is typically aerobic and an energy intensive process, mainly due to the required aeration. Alternative sustainable processes are sought, such as Microbial fuel cells (MFC) where electrogenic bacteria can degrade organic matter present in the waste stream while simultaneously generating electricity.

MFCs represent an emerging technology which may deliver the capability to reduce the pollution potential of low strength wastewaters (< 1500 mg COD l\(^{-1}\)) while generating electricity which could be used to self-power the process. Waste streams high in volatile fatty acids (VFAs) with high conductivity are particularly preferred substrate streams. These may include the effluent from two stage bio-hydrogen and bio-methane systems, which in this study were treated in a four-module tubular MFC (V=1 l) to reduce the chemical oxygen demand (COD) and recover further energy from the substrate. It was shown that the power increased with increasing organic loading rate (0.036-0.572 g sCOD l\(^{-1}\) d\(^{-1}\)), but COD removal efficiency decreased. The Coulombic Efficiency (CE) was found to decrease significantly at OLR > 0.6 g sCOD l\(^{-1}\) d\(^{-1}\) and the energy recovery was 92.95 J l\(^{-1}\) (OLR=0.572 g sCOD l\(^{-1}\) d\(^{-1}\)). Also, wash-down waters from a chilled food producing company were treated in the same tubular MFC, reducing the soluble COD content by 84.8%.

The low power (≈ 30 W m\(^{-3}\)) and cell potential (≈ 0.5 V) makes it necessary to investigate methods such as external capacitors, DC/DC converters or serial and parallel connection to improve the power quality. In this thesis, the use of the intrinsic capacitance was tested by switched mode, open and closed circuit (OC/CC) operation of a 2-module tubular MFC with high surface area carbon veil anode. The charge accumulated during OC and released when switched to CC was dependent on the external resistor (R = 100-3 kΩ) and duty cycle. Short period OC/CC switching further increased potential due to the pseudo-capacitance of the reactor, but only at the expense of energy efficiency, compared to continuous operation (CC) under constant load.

Another approach to enhance the practical implementation of MFCs is integration with other processes such as reverse electrodialysis to increase MFC’s cell potential or e.g. desalination. In this study a MFC was integrated with supported liquid membrane technology (SLM) for the first time, for the removal of metal ions of wastewater. A three chamber reactor, with a common cathode/feed phase containing 400 mg Zn\(^{2+}\) l\(^{-1}\), enabled
the simultaneous treatment of organic- and heavy metal containing wastewaters. The MFC/SLM combination produces a synergistic effect which enhances the power performance of the MFC significantly; 0.233 mW compared to 0.094 mW in the control. It is shown that the 165±7 mV difference between the MFC/SLM system and the MFC control is partially attributable to the lower cathode pH in the integrated system experiment, the consequent lower activation overpotential and higher oxygen reduction potential. The system demonstrates that within 72 h, 93±4% of the zinc ions are removed from the feed phase. A further study, with continuously operated cathode/feed chamber (100 mg Zn²⁺ l⁻¹), showed that an enhanced effect on increasing cell potential was possible and could also be maintained in continuous operation.
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<th>Description</th>
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<tbody>
<tr>
<td>[BuMelm][PF6]</td>
<td>Butyl-3-methyl-imidazolium hexafluorophosphate</td>
</tr>
<tr>
<td>[empa][NfO]</td>
<td>Ethylmethylpropylammonium nano fluoromethanesulfonate</td>
</tr>
<tr>
<td>Ac</td>
<td>Acetate</td>
</tr>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
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<tr>
<td>AD</td>
<td>Anaerobic Digester</td>
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<tr>
<td>AEM</td>
<td>Anion Exchange Membrane</td>
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<tr>
<td>AL</td>
<td>Activation Losses</td>
</tr>
<tr>
<td>An</td>
<td>Anode</td>
</tr>
<tr>
<td>BAEH</td>
<td>Poly(bis-phenol-A-co-epichlorohydrin)</td>
</tr>
<tr>
<td>BES</td>
<td>Bioelectrochemical System</td>
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<tr>
<td>BOD</td>
<td>Biological Oxygen Demand</td>
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<tr>
<td>Cat</td>
<td>Cathode</td>
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<tr>
<td>CC</td>
<td>Closed Circuit</td>
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<tr>
<td>CDI</td>
<td>Capacitive Deionization</td>
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<td>Cation Exchange Membrane</td>
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<tr>
<td>CF</td>
<td>Control Fridge</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotubes</td>
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<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
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<tr>
<td>CoTMPP</td>
<td>Cobalt tetramethoxyphenylporphyrin</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>CRT</td>
<td>Control Room Temperature</td>
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<tr>
<td>CV</td>
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<tr>
<td>D₂EHPA</td>
<td>Di-(2-ethylhexyl)phosphoric acid</td>
</tr>
<tr>
<td>DABCO</td>
<td>Quaternary 1,4-diazabicyclo-[2.2.2]-octane</td>
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<tr>
<td>DAF</td>
<td>Dissolved Air Flotation</td>
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<tr>
<td>ECE</td>
<td>Energy Conversion Efficiency</td>
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<tr>
<td>EDTA</td>
<td>Ethylenediamine tetraacetic acid</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
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<tr>
<td>FePc</td>
<td>Iron(II)phthalocyanine</td>
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<tr>
<td>FRA</td>
<td>Frequency Response Analyzer</td>
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<tr>
<td>GHG</td>
<td>Green House Gases</td>
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<td>Acronym</td>
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<tr>
<td>HRT</td>
<td>Hydraulic Retention Time</td>
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<td>I$_{avg}$</td>
<td>Averaged current</td>
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<tr>
<td>ICP-OES</td>
<td>Inductive Coupled Plasma Optical Emission Spectroscopy</td>
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<tr>
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<td>MDC</td>
<td>Microbial Desalination Cell</td>
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<td>Membrane Electrode Assembly</td>
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<tr>
<td>MREC</td>
<td>Microbial reverse-electrodialysis electrolysis cell</td>
</tr>
<tr>
<td>MRMC</td>
<td>Microbial reverse-electrodialysis methanogenesis cell</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>OC</td>
<td>Open Circuit</td>
</tr>
<tr>
<td>OCV/P</td>
<td>Open Circuit voltage/potential</td>
</tr>
<tr>
<td>OLR</td>
<td>Organic Loading Rate</td>
</tr>
<tr>
<td>OP</td>
<td>Overpotential</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
</tr>
<tr>
<td>P$_{avg}$</td>
<td>Averaged power</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate buffer saline</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PHA</td>
<td>Polyhydroxyalkanoates</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PPy-GO</td>
<td>Polypyrrole-graphene oxide</td>
</tr>
<tr>
<td>PS-b-PEO</td>
<td>Polystyrene-b-poly(ethylene oxide)</td>
</tr>
<tr>
<td>P$_{ss}$</td>
<td>Steady state power</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>Q-FPAE</td>
<td>Quaternary ammonium functionalized fluorinated poly(arylene ether)</td>
</tr>
<tr>
<td>R$_{CT}$</td>
<td>Charge Transfer Resistance</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>RED</td>
<td>Reverse Electrodialysis</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>$R_{\text{OHM}}$</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>$R_{\text{POL}}$</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>$R_{\Omega}$</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>$s\text{COD}$</td>
<td>Soluble Chemical Oxygen Demand</td>
</tr>
<tr>
<td>SLM</td>
<td>Supported Liquid Membrane extraction</td>
</tr>
<tr>
<td>SMEE</td>
<td>Switched Mode Energy Efficiency</td>
</tr>
<tr>
<td>TBP</td>
<td>tri-n-butylphosphate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TOPO</td>
<td>tri-octylphosphine oxide</td>
</tr>
<tr>
<td>$U_{\text{ss}}$</td>
<td>Steady state voltage</td>
</tr>
<tr>
<td>VFA</td>
<td>Volatile Fatty Acids</td>
</tr>
<tr>
<td>WDE</td>
<td>Warburg Diffusion Element</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
<tr>
<td>ZVI</td>
<td>Zero Valant Iron Process</td>
</tr>
<tr>
<td>$Z_{W}$</td>
<td>Warburg Diffusion Element</td>
</tr>
</tbody>
</table>
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Membrane area</td>
<td>m²</td>
</tr>
<tr>
<td>CPE\textsubscript{biofilm}</td>
<td>Fitting constant phase element value for the biofilm</td>
<td>F s(^{(\alpha-1)})</td>
</tr>
<tr>
<td>CPE\textsubscript{HL}</td>
<td>Fitting constant phase element value for Helmholtz layer</td>
<td>F s(^{(\alpha-1)})</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>m s(^{-2})</td>
</tr>
<tr>
<td>E\textsuperscript{0}</td>
<td>Standard redoxpotential pH=7</td>
<td>V</td>
</tr>
<tr>
<td>E\textsubscript{0}</td>
<td>Potential amplitude</td>
<td></td>
</tr>
<tr>
<td>E\textsubscript{EMF}</td>
<td>Standard cell electromotive force</td>
<td>V</td>
</tr>
<tr>
<td>E\textsubscript{COD}</td>
<td>Energy production per COD consumed</td>
<td>Wh g sCOD(^{-1})</td>
</tr>
<tr>
<td>E\textsubscript{EMF}</td>
<td>Cell electromotive force</td>
<td>V</td>
</tr>
<tr>
<td>E\textsubscript{ON/OFF}</td>
<td>Energy obtained during on/off operation</td>
<td>Wh</td>
</tr>
<tr>
<td>E\textsubscript{SS}</td>
<td>Energy during obtained during steady state operation</td>
<td>Wh</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
<td>C mol(^{-1})</td>
</tr>
<tr>
<td>MM</td>
<td>Molare Mass</td>
<td>g mol(^{-1})</td>
</tr>
<tr>
<td>n</td>
<td>Number of electrons per reaction mol</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Membrane permeability</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>q</td>
<td>Flow rate</td>
<td>l s(^{-1})</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>v\textsubscript{an}</td>
<td>Volume of the anode chamber</td>
<td>l</td>
</tr>
<tr>
<td>v\textsubscript{react}</td>
<td>Reactor volume</td>
<td>l</td>
</tr>
<tr>
<td>W</td>
<td>Work</td>
<td>J</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Measure of semicircle depression</td>
<td></td>
</tr>
<tr>
<td>(\Delta G)</td>
<td>Gibbs free energy</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta G\textsubscript{r}^0)</td>
<td>Standard Gibbs free energy</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Membrane conductivity</td>
<td>S cm(^{-1})</td>
</tr>
<tr>
<td>(\phi)</td>
<td>Phase shift</td>
<td>rad s(^{-1})</td>
</tr>
<tr>
<td>X</td>
<td>Conductivity</td>
<td>S cm(^{-1})</td>
</tr>
<tr>
<td>(\omega_{\text{max}})</td>
<td>Angular frequency</td>
<td>rad s(^{-1})</td>
</tr>
</tbody>
</table>
1. Introduction

Climate change and the need for alternative energy and clean water are important issues in the 21st century. Climate change caused by the emission of greenhouse gases (GHG) is a widely accepted global problem. Today 80% of the global energy consumption is based on fossil fuels, leading to the emission of CO₂ which is responsible for the majority of the global greenhouse gases. The CO₂ concentration in 2012 was about 40% higher than in the mid-1800s, with further significant increases in N₂O and CH₄, which makes human influence on the climate change clear (IEA, 2013). Some of the impacts of the high GHG emission might become apparent later and given the long lifetime of CO₂ in the atmosphere, even after stabilization of the atmospheric concentration of CO₂, anthropogenic warming and sea level rise would continue for centuries due to the time scales associated with climate processes and feedbacks (IEA, 2013). The emission of GHG is mainly attributed to the use of energy, with minor contributions from agriculture and nearly two thirds of the global GHG emission originates from ten countries. GHG emissions are led by China (25.4%) and US (16.9%) (IEA, 2013).

Another important factor and most essential resource is water. Its consumption is increasing rapidly due to increasing population and demand for food and products. Fresh water consumption increased by more than double that expected with respect to the population increase between 1900 and 1995, which led to the development of new technologies for wastewater reuse and sea and brackish water desalination (Macedonio et al., 2012). Today one third of the population is living in countries considered to experience water emergency, which will rise to two third in 2025. Hence there is an urgent need for water reuse for irrigation, power plant cooling, industrial process water and the development of new less energy consuming wastewater treatment technologies.

In the UK, water companies consumed 1% of the total electricity usage (7.703 GWh in 2005/2006) and produced 4.15 MtC of CO₂/year (KTN, 2008). 586 kWh were required to treat 1 ML water and 634 kWh to treat 1 ML sewage, with most of the energy consumed by the treatment used by activated sludge aeration (55.6%), followed by the costs for influent pumping, heating and primary settlement costs (KTN, 2008). In the UK, water companies are committed to delivering carbon neutral wastewater treatment by 2020, which will involve a reduction in carbon emissions of between 1.1–1.6 Mt of carbon per year. To achieve this, a change from the current aerobic wastewater treatment
technologies towards alternatives, which are not only low energy requiring processes but also energy producing processes, might be needed (Oh et al., 2010). One approach to increase the sustainability of conventional aerobic wastewater treatment plants is to use the sludge as a raw material for biodiesel production as Fatty Acid Methyl Ester (FAME). The lipid fraction of the waste activated sludge can be transesterified to produce FAME. Furthermore the fraction of lipids was increased when using microalgae in aerobic reactors, which also increases nutrient removal (Velasquez-Orta, 2013).

The activated sludge systems is the conventional wastewater treatment method, but the operating costs of wastewater treatment plants is forecasted to increase (Escapa et al., 2014) due to increasing electricity costs. The European market of municipal water and wastewater treatment predicts a growth rate of 4.1% per year. In general, aerobic treatment produces large amounts of sludge, for which disposal costs will have to be paid. Theoretically, there is enough energy in the wastewater to run the whole process with net energy surplus, but new processes and technologies need to be developed to exploit all the potential energy in waste (Escapa et al., 2014).

One of these technologies could be bioelectrochemical systems (BES), including microbial fuel cells, which could contribute to both, wastewater treatment and reducing energy costs by bio-energy generation and value added processes.

In a microbial fuel cell system, electrical current is directly generated from bacteria, which act as a catalyst in the oxidation of biodegradable organic matter in an anodic chamber. The microbial catalysis is characterized by an electrogenic metabolism with an anode electrode as the electron acceptor. The catalysis also produces a protonic counter current \([\text{H}^+]\) to a cathode, so maintaining charge balance in the cell. A MFC can use organic components from wastewater of other biodegradable material as a fuel and may therefore simultaneously treat a waste stream and produce electricity. MFCs are therefore able to convert low grade chemical energy in waste to electricity. Although the ability of bacteria to produce electricity was reported by Potter (1911), significant interest has only been rekindled in the past 15 years, during which the number of articles on the topic exponentially increased (Pant et al., 2010b).
1. Introduction

The main oxidation products of anode respiring bacteria are protons, electrons and carbon dioxide. The electrons reach the cathode by an external circuit and combine with the protons which diffuse through a separator or membrane and combine with oxygen from the air. In the anode chamber, electroactive anaerobic bacteria growing on the electrode can use the anode electrode as their final electron acceptor (see Figure 1-1).

As the conventional activated sludge process requires 0.3 kWh m$^{-3}$ for aeration and twice as much for other processes such as pumping, the greatest benefit of anaerobic technologies such as MFCs and anaerobic digestion (AD) are the cost savings due to the avoidance of aeration. In theory domestic wastewater contains about 2 kWh m$^{-3}$, but only a small amount can be recovered (12 W m$^{-3}$) in an MFC as reported by Heys et al. (2011), which is equivalent to 0.07 kWh m$^{-3}$. To commercialize MFCs the initial acquisition costs has to be reduced and/or the conversion of organic matter into electricity has to be optimized so that reasonably short payback periods can be achieved to make them more likely to be implemented. Also it has to be kept in mind that manufacturing costs are likely to decline if the number of produced systems increases. Waste treatment using MFCs might present advantages such as the ability to treat low strength organic waste streams and the concomitant production of electricity, directly without further losses compared to other energy to electricity conversion systems, furthermore the reduction in sludge production and the necessity for forced aeration and possibly heating.

It has been shown that MFCs are able to operate over a broad temperature range with comparable efficiency (Michie et al., 2011a, Michie et al., 2011b, Jadhav and Ghangrekar, 2009). Besides, electrogenic bacteria can degrade various substrates (e.g. acetate, propionate, butyrate, glucose, saccharose, cellulose, …) and the bacteria themselves act as

![Figure 1-1: Schematic illustration of a microbial fuel cell.](image-url)
self-regenerating sustainable biocatalyst. Industrial wastewater could also be an ideal candidate, as higher conductivities are essential for efficient power production and typical domestic wastewater conductivities are low, only around 1.80 ± 0.54 mS cm$^{-1}$ (Ahn and Logan, 2010). Hence MFC systems could be implemented in a decentralized manner, to treat waste stream anaerobically where they are produced and discharged.

Even though wastewater treatment has the potential to become a net energy producer (McCarty et al., 2011), it is also quite clear that microbial electrochemical systems such MFCs and MEC will not be able to rapidly replace the current treatment systems consisting of primary and secondary treatment (Escapa et al., 2014). Their application might be complimentary to the existing treatment system or integrated into the process for example for nutrient recovery, such as struvite. Another approach would be the integration with anaerobic processes such as anaerobic digestion and dark fermentation (Guwy et al., 2011).

In general Bioelectrochemical systems research activities have been shifting from wastewater treatment towards a much broader field of application. It has been shown that other reactions than the reduction of oxygen can be carried out on the cathode such as the reduction of metal ions, organic components or bio-cathode systems for nitrate reduction. Furthermore, additional power can be supplied to produce hydrogen on the cathode (Microbial electrolysis cell MES) or bacteria can be used to synthesis higher valuable components. The possibilities mentioned, as well as other approaches, will be discussed in the following section to give a short overview on the broad field of BES.

A particular type of microbial fuel cell is the sediment or benthic MFCs, where bacteria oxidize substrate in the sediment and dissolved oxygen in the seawater is reduced on the cathodic side. This systems represent a very promising technology to power marine sensors (Donovan et al., 2011). Also photosynthetic reaction was coupled with microbial electricity production resulting in microbial solar cells, where algae, higher plants or photoautotrophic bacteria convert solar energy to organic matter (Deng et al., 2012, Wang and Ren, 2013). Plant MFCs use the organics secreted from their roots (rhizosphere) to feed electrogens and therefore indirectly utilize solar energy. Different plants such as *P.setaceum* (Chiranjeevi et al., 2012), reed mammagrass (Strik et al., 2008) and rice (Oryza sativa L.)(Chen et al., 2012c) have been used in plant-MFC.
Another area of application could be bioremediation of aquatic sediments and groundwater (Lovley and Nevin, 2011). The anaerobic oxidation of organic contaminants in MFCs has been shown for pyridine (Zhang et al., 2009a), 1,2-dichlorethane (Pham et al., 2009), or phenol (Luo et al., 2009). Another approach is associated with biocathodes, which have been used to reduce nitrate (Wrighton et al., 2010) and perchlorate (Butler et al., 2010). Apart from the above mentioned nitrate reduction, other nutrients can also be removed and recovered in BES. The recovery of phosphate and nitrogen is especially of interest, due to their broad use as fertilizers. Biological phosphorus removal is exclusively through precipitation and presents more difficulties than nitrogen. Nitrogen removal was recently also shown to be possible in the thermophilic range relevant to warm industrial wastewater streams (Lopez-Vazquez et al., 2014). The removal of phosphorus as struvite on the cathode has been investigated from urine (Zang et al., 2012) and swine wastewater (Ichihashi and Hirooka, 2012).

One approach is the coupling of wastewater treatment with the production of valuable products at the cathode. Apart from hydrogen, also peroxide (Fu et al., 2010, Modin and Fukushi, 2012) and caustic soda (Rabaey et al., 2010) were produced in microbial electrolysis cells. Additionally, treatment of specialized wastes such as the removal of azo dyes was reported in a biocathode chamber of an electrolysis system (Wang et al., 2013c). For the production of hydrogen an additional external potential of 0.6 to 1.0 V needs to be applied, which is significantly lower than in water electrolysis (1.8-2.0 V) (Liu et al., 2005).

Even though microbial electrosynthesis requires additional power, it is promising as it offers the possibility to reduce carbon dioxide by converting it into organic compounds by abiotic or biotic catalysts, whereby latter might be better (Lovley and Nevin, 2011). Acetate and 2-oxo-butyrate were produced by using Sparomusa ovata using the cathode as electron acceptor (Nevin et al., 2010). Ethanol was produced from glycerol by engineered electrogenic bacteria Shewanella oneidensis (Flynn et al., 2010), as well as from acetate (Steinbusch et al., 2009).

Furthermore medium chain fatty acids caproate and caprylate (precursors for liquid fuels) were produced with a mixed culture biofilm on the cathode (-0.9 V) of a bioelectrochemical system (Van Eerten-Jansen et al., 2013). Srikanth et al. (2012) reported the production of polyhydroxyalkanoates (PHA) at a microaerophilic reduction microenvironment biocathode. Microbial electrosynthesis shows great promises not least because of genetically modified organism. However, many economic challenges have to
be solved as the process competes with well established methods for the production of certain chemicals and also techniques to harvest or remove the chemicals produced need to be found. Another operational for MFCs are biosensors. The current or voltage response of MFCs can be correlated with the concentrations of certain target species. MFC to sense BOD (Di Lorenzo et al., 2009b, Di Lorenzo et al., 2009a), toxicity (Shen et al., 2012) as well as VFAs (Kaur et al., 2013) were developed.
1. Introduction

1.1 Objective of the thesis

The broad aim of reported work in this thesis was to enhance the performance of MFCs while simultaneously improving the function of waste stabilization that they promise. In as much, specific objective are presented which reflect the broad aim. The objectives include investigating operation of MFCs on real wastewater; improving the cathode performance with respect to material choice; and investigating increased power quality, particularly voltage generation, by operating strategy and by exploring an integration approach to increase their scope for application. The specific objectives are therefore listed as follows:

- To investigate the effluent polishing capability of a tubular MFC design processing a real wastewater under different operation strategies.

- To investigate the integration of MFCs into a system with other anaerobic bioprocesses to increase the energy recovery.

- Identification of strategies to increase MFCs applicability by increasing the cell voltage and the concomitant power output from MFCs. More specifically, to investigate using capacitance and intermittency to increase voltage or by integration with other complementary systems to enhance the usability of the power produced.

- To investigate electrode systems to enhance the catalytic oxygen reduction reaction. The significant challenge of PGM replacement, without comparative loss of performance, will be addressed from the point of view of empirical studies on catalyst/binder systems to reduce the overpotentials incurred in the ORR.

- To investigate the benefits of integrating bioelectrochemical systems capable of removing heavy metal ions, with MFCs. The technology of liquid membrane permeation specifically should be integrated into a microbial fuel cell system in order to extend the applicability and explore possible synergistic effects.
1.2 Organization and structure of the thesis

Chapter 1 gives the broader context of the presented work and introduces the reader to the main principals of microbial fuel cells and the extent to which this work is aiming to improve the current system and investigate novel approaches to overcome some of the existing limitations.

The second chapter represents an overview of the current state of the art from the literature on microbial fuel cells with the main focus placed on the literature relevant to the work presented in this thesis. It also further explains the principles of other fields, which are not directly related to BES, such as supported liquid membrane permeation (SLM) and ionic liquids (IL).

The chapters 4-8 present the results obtained in the experimental studies undertaken and all the methods and materials are summarized in a separate chapter 3 (Materials and Methods). Chapter 4 deals with use of real waste streams in MFCs and the results presented in the chapter 5 considers OC/CC duty cycling as an operating strategy to increase the cell voltage. The results of Ionic liquid based binder systems with two different oxygen reduction catalyst are presented in chapter 6. The last two results chapters deal with the integration of supported liquid membrane permeation for heavy metal (zinc) recovery in an MFC; with a proof of concept study in chapter 7 and further investigations regarding continuous operation in chapter 8. Chapter 9 presents the conclusion drawn and future projections for the work.

Appendix A provides further tables for the work presented in chapter 4 and appendix B includes a list of the scientific output, including poster and oral presentation at conferences and journal publication derived from this study.
2 Literature Review

In a Microbial Fuel Cell organic substrate is oxidized by electrogenic bacteria, which can use the anode as a final electron acceptor, enabling them to produce electrical current. The transfer of electrons from the substrate to the anode occurs through the metabolic actions of bacteria (typically in a biofilm), and through various electron transfer mechanisms:

- membrane spanning cytochromes (Bond and Lovley, 2003), and/or
- electrically conductive pili or nanowires (Gorby et al., 2006, Reguera et al., 2005) or
- through the involvement of self-excreted redox-mediators or added redox-mediators (Rabaey et al., 2005, Tang et al., 2010, Velasquez-Orta et al., 2010) or via the oxidation of reduced primary metabolites (Patil et al., 2012, Rosenbaum et al., 2006).

Even though the technology is promising, there are bottlenecks such as the low power produced and others which will be addressed in this chapter.

2.1 Voltage generation and principal thermodynamic considerations

The generation of electricity from electrogensis will only occur if the reaction is thermodynamically favorable. Hence the Gibbs free energy needs to be endergonic ($\Delta G < 0$) for the reaction to occur spontaneously. The work (J) that can be done in an MFC is related to the cell electromotive force ($E_{\text{EMF}}$; potential difference between anode and cathode) through the relationship given in Equation 1 (Logan et al., 2006a):

\[
W = nFE_{\text{EMF}} = -\Delta G_r
\]

Where the electromotive force of the cell is given by:
2. Literature Review

\[ E_{\text{EMF}} = E_{\text{EMF}}^0 - \frac{RT}{nF} \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]  
\[ \text{Equation 2} \]

With \[ E_{\text{EMF}}^0 = -\frac{\Delta G_r^0}{nF} \]

\[ \Delta G_r^0 \quad \text{Gibbs Free Energy under standard conditions (J mol}^{-1} \text{)} \]

If we assume a microbial fuel cell is fed with acetic acid and has an air cathode, the thermodynamic (maximum theoretical) cell potential can be calculated from the standard redox potentials, which refer to the standard conditions of \( T=295K, p_{H_2}=1 \text{ bar} \) and \( pH=1 \).

The reactions taking place on the anode and cathode are the following:

**Anode:** \[ 2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \]  
\[ \text{Equation 3} \]

**Cathode:** \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  
\[ \text{Equation 4} \]

To adapt the cell potential to the actual conditions, the Nernst equation can be used:

\[ E_{\text{An}} = E_{\text{An}}^0 - \frac{RT}{nF} \ln \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{HCO}_3^-]^2 [\text{H}^+]^4} \right) \]  
\[ \text{Equation 5} \]

\[ E_{\text{Cat}} = E_{\text{Cat}}^0 - \frac{RT}{4F} \ln \left( \frac{1}{p_{\text{O}_2} [\text{H}^+]^4} \right) \]  
\[ \text{Equation 6} \]

The power produced by an MFC has increased by three orders of magnitude in the last 15 years. However, there are limitations which hinder their implementation at larger scale. As microbial fuel cell technology represents an interface between different research areas, including microbiology, electrochemistry, material research and engineering, there are many ways by which performance improvements have been made, such as by improving reactor configurations, enrichment of electrogentic bacteria and materials used. However, one of the major concerns is the low cell potential in MFCs. The maximum thermodynamic cell potential is given by the standard redox potentials of acetate and oxygen and by using Equation 5 and 6, given that the oxygen partial pressure is 0.2 atm and assuming an acetate concentration of 16.69 mM and a pH value of 7, the maximum cell potential can be calculated as:

\[ E^* = E_{\text{cathode}}^* (0.805 \text{ V}) - E_{\text{anode}}^* (-0.300 \text{ V}) = 1.105 \text{ V} \]  
\[ \text{Equation 7} \]

However, there are losses which lower the cell potential from the theoretical, namely electrode overpotentials (OP), ohmic losses, activation and mass transfer losses (Logan, 2008).
In a typical air-cathode MFC, the activation losses (AL) are higher on the cathode than on the anode (Rismani-Yazdi et al., 2008). On the anode the biofilm act as self-generating biocatalyst which lowers the overpotential. Activation losses arise from the initiation of oxidation or reduction reactions and these losses can be lowered by a catalyst or by elevated temperatures and are also influenced by polarization and the double layer capacitance. In a tubular MFC and in general, the activation overpotential on the cathode is significantly higher as can be seen in Figure 2-1 region 1. Also the electrode overpotential is more pronounced at low current densities, where ohmic losses dominate in the higher current region 2, showing an almost linear decrease. Low activation losses can be achieved by increasing the operation temperature, improving the catalyst or increasing the electrode surface area (Logan et al., 2006a).

\[ E_{MFC} = E^0 - (\sum OP_{anode} + \sum OP_{cathode} + I \times R_H) \]  

Equation 8

Ohmic losses are governed by the distance between anode and cathode, the electrode and solution conductivity and membrane or separator if present in the system. The system design and materials can significantly influence the ohmic resistance in an MFC, but other
factors such as conductivity will be intrinsic to the components in the wastewater. In the third region the voltage drops at high current due to the resulting mass transfer limitations (concentration losses). In this region the transfer of the reactants to and products from the electrode become limiting.

Hence the anodic and cathodic potentials set the limit for the maximum achievable cell potential and therefore power generation. However, apart from the losses mentioned above, bacteria metabolism is also associated with losses. Bacteria transfer electrons from the substrate with a low potential through the electron transfer chain and different redox processes and cell cytochromes to the final electron acceptor. Hence electrons will only be transferred from lower potential through cytochromes to a higher reduction potential. The energy gain for the bacteria is determined by the anode potential, hence the higher potential difference between the substrate and the anode potential the higher the energy gain for the bacteria. However, this will lower the MFC cell potential, so from this point of view the potential of the anode should be as low as possible (Logan et al., 2006a).

### 2.2 Impedance spectroscopy in Microbial fuel cells

Internal resistance of a microbial fuel cell as well as the distribution into activation losses (charge transfer/polarization resistance, double layer capacitance), ohmic losses and diffusion related losses can be determined by using electrochemical impedance spectroscopy (EIS). EIS has been used to evaluate the performance of MFCs cell with and without bacteria, in open or closed circuit, as well as for investigating specific system components such as cathode, anode or the separator. Even though microbial fuel cells are complex system, quantitative interpretation of the system components can be obtained by fitting the spectrum to meaningful equivalent circuits (Sekar and Ramasamy, 2013). One of the biggest advantages is the non-destructive measurement, which allows a system to be studied without significantly disturbing its operation; this requires low amplitude sinusoidal disturbances, typically of the potential (< 15 mV) to be applied. This is assumed to not disturb the biofilm and the operating MFC (Dominguez-Benetton et al., 2012). Commonly used electric equivalent circuits EEC are presented in Figure 2-2, for half cell (a) and full cell (b) fitting. These simple modules consist of the ohmic resistance ($R_{\text{OHM}}$), the polarization resistance ($R_{\text{POL}}$) or charge transfer resistance ($R_{\text{ct}}$), if the measurement is carried out under open circuit conditions. The double layer capacitance is represented as a
constant phase element (CPE) and replaces the capacitor (double layer capacitance). A constant phase element is required to account for the semicircle depression in the Nyquist plot caused by the inhomogeneity of anode surface (surface roughness, porosity, non-uniform current distribution), which may be considered to be a distributed capacitance. An ideal flat surface (2-dim.) will appear as a perfect semi-circle in the Nyquist plot and a capacitor could be used instead. However, in practice, semicircle depression will occur and a CPE will be used in parallel with the polarization resistance.

Figure 2-2: Equivalent circuit models (ZView 2™) for half cell measurements (a) and whole cell MFC measurements (b).

Several studies have investigated the anode impedance in half cell conditions (3 electrode mode), where the model presented in Figure 2-2 (a) is the most common used. In certain cases, when diffusion is dominant (45°) a Warburg diffusion element ($Z_W$) is included in the circuit (in series with $R_{CT}$). Several half cell studies of the anode have been carried out; a previous study has shown that the growing biofilm significantly decreases the charge transfer resistance. At the beginning of the biofilm formation the charge transfer resistance decreased by over 70% in the first eight days (Ramasamy et al., 2008). Similar observations were made by Borole et al. (2010), where the anode impedance decreased from 296.1 Ω to 36.3 Ω in the 43 days of operation, with a mixed culture biofilm. It was also observed that the cathode impedance (air cathode with Pt catalyst) increased during this period of time from 1.27 Ω (24 days) to 15.1 Ω (165Ω). Regarding the capacitance of the anode it was observed, that this factor increased by two orders of magnitude from 0.007 F (day 61) to 0.45 F (day 165) and it was concluded that the behavior of the anode double layer changed from a non-ideal capacitive behavior to an ideal capacitor over this time frame. Manohar et al. (2008b) studied the anodic impedance with and without a *Shewanella oneidensis* MR-1 biofilm and found that the capacitance only slightly increased (9.22*10^{-4} F without and 9.70*10^{-4} F with the bacteria). Kim et al. (2011b) monitored the bacterial adhesion and biofilm maturation by observing changes in the double layer capacitance with *Pseudomonas aeruginosa* PA14 wild type; the model presented in Figure 2-2 (a) was used in this study. Apart from changes in the double layer capacitance, the
effect of the electrolyte pH (He et al., 2008) and the addition of mediators (Ramasamy et al., 2009) have also been investigated.

EIS was also used to investigate the cathode (Martin et al., 2011, Zhang et al., 2012e) as well as biocathodes (Ter Heijne et al., 2010) in half cell conditions.

These studies have shown that the anodic capacitance is influenced by the several factors including the biofilm and electrolyte composition, hence both anodic and cathodic capacitance has to be taken into account when investigating the total capacitance of the microbial fuel cell, as presented in chapter 5.

Hence, EIS presents a powerful tool for investigating the impedance of different MFC components as well as the whole reactor impedance. One of the components studied was the membrane or separator; Wei et al. (2013) have shown using EIS that a wipe cloth separator lowers the current due to diffusion limitations. EIS is also useful to observe changes in the membrane conductivity which occurs with time during operation, and which has not yet been investigated in MFCs.

2.3 Membranes and separators

Several reactor configurations have been developed and published by others (Janicek et al., 2014), including single- and dual chamber MFCs as well as tubular and flat plate MFCs. Many of these configurations have ion exchange membranes (cation-exchange membranes CEM, anion-exchange membranes, bipolar membrane) or other separators (microfiltration, ultrafiltration, glass fibers, porous fabrics), mainly to avoid the intrusion of oxygen into the anaerobic cathode chamber. The intent is to ensure that all the electrons generated by electrogenic bacteria are transferred to the electrode instead of directly using oxygen as terminal electron acceptor. A membrane or separator should also avoid substrate cross-over to the cathode. The substrate can be oxidized on the cathode surface by aerobic bacteria which can also reduce the CE as it creates an internal short circuit (Hou et al., 2011, Leong et al., 2013). Furthermore, the growth of aerobic bacteria on the cathode can lead to bio-fouling, which was found to initially enhance the power but lowers the power output in long term operation due to the lower active surface area and the decreased oxygen diffusion (Chung et al., 2011). However, it should be kept in mind that membranes and separators are also associated with a higher internal cell resistance.
which can cause pH splitting; where the protons accumulate in the anode chamber (resulting in lowered pH) while the cathode chamber suffers from proton depletion (raising pH). This effect is especially pronounced if CEM are used, as the concentration of other cations such as Na$^{2+}$ or K$^+$, may be present in significantly higher concentrations than H$^+$ (4-5 orders of magnitude) and are therefore more likely to be transferred through a cation exchange membrane (Rozendal et al., 2006), showing that it is important to guarantee a certain proton concentration. Lower pH values affect the ORR positively by reducing the cathodic overpotential. According to the Nernst equation this amounts to an increase of 59 mV for each pH unit, resulting in higher cell potential and power output. This is in accordance with the findings from Zhuang et al. (2010) who operated a MFC with high anodic pH (10) and low cathodic pH (2) to achieve higher power densities and an open circuit potential (OCP) of 1.04 V with iron(II) phthalocyanine (FePc) as cathode catalyst or Erable at al. (2009) who observed the same effect with a low pH air cathode using Pt as the catalyst. Hence, a low cathodic pH value can be used to increase the cell potential but might not be sustainable as the protons will be depleted with time. Therefore it is necessary to find a more sustainable way to keep the pH at the cathode low; probably through combination with another process, where low pH values are not desired (such as in the feed phase of liquid membrane separation) or one of several other processes, which would otherwise need the addition of buffer or alkaline solution.

2.4 Catalyst and binder materials for the oxygen reduction reaction in Microbial fuel cells

As mentioned in paragraph 2.1, the activation losses are more pronounced on the cathode, especially if oxygen is used as terminal electron acceptor. Hence the optimal combination of catalyst and binder are important to minimize these losses in order to achieve cell potentials closer to the thermodynamic maximum. In general a catalyst is used to increase the reduction rate of oxygen.
2. Literature Review

2.4.1 Catalysts

In air cathode MFC systems, oxygen acts as the electron acceptor and combines with two protons to form water (Liu and Logan, 2004). While before 2010 ferricyanide was commonly used in MFC system to carry out the cathodic reduction reaction in MFC, the reduction is now typically carried out using oxygen in air, which is reduced on the cathode to form water. Hexacyanoferrate (mediator; $E^0=0.358 \text{ V}$) and permanganate (oxidant; $E^0=1.07 \text{ V}$) result in reasonable high cell potential and faster reduction kinetics but are not considered to be sustainable for most perceived industrial applications and would need to be replenished, replaced or re-oxidized as it is consumed. Oxygen in air is widely considered to be the most plausible terminal electron accepter for MFCs, because of the benign environmental consequences of its use compared with other oxidants, particularly in scale-up. Oxygen in air is cheaply and easily available; however Platinum (Pt) the catalyst commonly used for this reaction is expensive.

The main disadvantages of using such an environmental friendly reducing agent are the high costs, the still relatively high activation overpotential and low kinetic rate of the reduction reaction, due to this and other parameters it has been suggested, that the cathode is the current limiting electrode in existing MFC systems (Fan et al., 2008b, Rismani-Yazdi et al., 2008). However, there is a need to use a catalyst as the reaction cannot be carried out with reasonable velocity without a suitable catalyst.

![Figure 2-3: Oxygen reduction activity plotted as a function of the oxygen binding energy for different metal catalysts after (Nørskov et al., 2004).](image)
2. Literature Review

Figure 2-3 shows several metal catalysts for the ORR and the correlation between the catalytic activity and the oxygen binding energy. It can be seen that Platinum Pt has the highest catalytic activity, followed by other expensive metals such as Pd. For the oxygen reduction reaction to occur, all educts need to meet on the catalyst surface at a three phase interface. Protons from the electrolyte (liquid) and oxygen from the gas phase need to accept electrons at the solid catalytic surface. The ORR exhibits a standard redox potential of $E^0=1.23$ V. In MFCs the pH will be around 7 and the reduction potential will be significantly lower. Furthermore there are two possible reduction pathways; a 4-electron associative mechanism and a 2-electron dissociative mechanism for the reduction of oxygen (Rismani-Yazdi et al., 2008).

4-electron pathway: $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O \quad E^0=0.816$ V

2 electron pathway: $2 O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O_2 \quad E^0=0.295$ V

Kinetic losses are the main challenge, because a one order of magnitude improvement only results in an increase of 60-70 mV and the potential has been proposed to be a function of the Gibbs free energy of oxygen adsorption (Debe, 2012).

One possible way to enhance the ORR would be to increase temperature. Hence one disadvantage compared to hydrogen fuel cells is that MFCs may need to operate at ambient temperature, whereas PEM-fuel cells operate at around 70-80 °C. Furthermore the pH value in MFCs is around pH=7 and therefore the proton concentration can easily limit the ORR. The oxygen must diffuse through the cathode and its associated materials, to be consumed at the 3-phase interface, as oxygen in the anolyte will be preferentially used as an electron acceptor because of the higher energy gain bacteria receive by using oxygen (aerobic respiration) as electron acceptor instead of the anode electrode. Oxygen intrusion will adversely affect the CE.

The low overpotential of Pt compared to other catalysts makes it the most commonly used catalyst for the ORR in MFCs. Apart from Pt, Cu and Au-coated copper have been tested (Kargi and Eker, 2007) as has lead dioxide coated electrodes (Morris et al., 2007). However, Au is also relatively expensive and PbO$_2$ requires special binders to avoid being leached from the cathode. Because of the high costs of Pt (1276 $/oz (Matthey, 2014)), several less costly catalysts have been tested as ORR-catalyst in MFCs, including Cobalt and Iron containing macrocycles. Iron(II)phthalocyanine (FePc) and cobalt tetramethoxyphenylporphyrin (CoTMPP) were tested and resulted in similar OCP of 1.07 V
(FePc) and 1.10 V (CoTMPP) (Zhao et al., 2005a). In this study the performance of the cobalt based material was slightly better, which was attributed to a possible stronger back bonding of oxygen. FePc and CoTMPP, FeCoTMPP and CoPc and FeCuPc have also been tested (HaoYu et al., 2007). In contrast to the study by Zhao et al. (2005a), Hao Yu et al. (2007) achieved a higher power density (634 mW m$^{-2}$) with FePc-KJB than with commercial Pt cathodes (593 mW m$^{-2}$).

All the macrocycle based catalysts are significantly less expensive than Pt, but have been shown to have certain limitations. It was found that the presence of Cl$^-$ ions in the electrolyte can block the active sites of those Pc- and TMPP-based catalyst and more importantly they are sensitive to high cathodic pH, a situation that can easily occur in MFCs (Rismani-Yazdi et al., 2008). Another study has shown that FePc is better than Pt in terms of catalyzing the reduction of other organic compounds (substrate crossover) and causes reduced internal currents; further it was found that the presence of sulphide inhibited the catalysis at both Pt and FePc (Harnisch et al., 2009).

Recently Nguyen et al. (2014) tested two new iron-chelat catalysts, namely ferric ethylenediamine-N,N′-bis (2-hydroxyphenylacetic acid) (NaFeEDDHA, NaFeE) and sodium ferric diethylene triamine pentaacetic acid (NaFeDTPA, NaFeD) in combination with carbon black and carbon nanotubes. FeE in combination with CNTs resulted in a slightly lower catalytic performance than Pt. FeE/CNT was active as cathodic catalyst and its performance was just slightly lower than that of Pt/C catalyst.

Since about 2010 the trend has been towards functionalized/modified carbon nanotubes and graphene. The electrocatalytic activity of iron and nitrogen functionalized graphene has been investigated and resulted in a 2.1 times higher power than with Pt (Li et al., 2012), however, the preparation is relatively costly as thermal polymerization at 550 °C is required. Also, a nano-composite of cobalt oxide and nitrogen doped graphene was tested in an MFC (Li et al., 2012, Feng et al., 2011, Liu et al., 2013a). Many studies deal with graphene based electrocatalysts, which display promising performance due to their high electrical conductivity, large specific surface areas and the functional groups which can be in-cooperated; but some challenges in terms of the ORR activity and their stability still remain (Zhu and Dong, 2013). Single wall and multiwall carbon nanotubes (CNT) modified cathodes were tested as a cathode catalyst by Wang et al. (2011a), and electrospun carbon nanofibres activated with KOH and CO$_2$ gas resulted in a higher surface area and catalytic activity (Ghasemi et al., 2011).
Plain activated carbon has been used in several studies and showed promising results due to the higher active surface area provided. Different types of activated carbon and different preparation methods have been used. Pant et al. (2010a) used a VITO™ activated charcoal electrode without any other catalyst, pressed onto a mesh current collector. Also, a nickel foam cathode with AC carbon and PTFE as a binder was developed and was found to be 30 times cheaper than a Pt-catalyzed electrode and resulted in only minor losses in comparison (1190 mW m\(^{-2}\) nickel foam vs 1320 mW m\(^{-2}\) Pt (Cheng and Wu, 2013)). The long term stability of AC carbon cathodes with different diffusion layer porosities (30% and 70%) were tested by Zhang et al. (2011) and their results showed a decreased performance after 1 year due to an increase in the diffusion resistance. Watson et al. (2013a) treated three different types of activated carbon (precursor materials: bituminous, peat, and hardwood) with ammonia gas, which resulted in an increased ORR activity attributed to an increase in nitrogen and a decrease in acidic oxygen surface functional groups.

These examples show that carbon nanotubes, graphene and activated carbon offer many possibilities in terms modification and functionalization, which are also associated with additional costs. Furthermore only CNTs have been used at smaller scale for commercial application, as the production processes are costly (chemical vapor deposition, laser deposition and other methods).

In this context it should be mentioned that microorganism were recently found to promote electron transfer to oxygen. Bacteria were found to significantly reduce the overpotential of the four electrode reaction, although the mechanism requires further study. One proposed pathway might be linked to the metabolic activity of the bacteria and another involves the bacterial excretion of redox-active compounds such as Quinones (Freguia et al., 2010). A lower pH and elevated temperature were found to be beneficial for the bacteria catalyzed ORR (Strik et al., 2013).

This section on catalysts for the oxygen reduction reaction (ORR) is a short excerpt from studies on ORR catalysts in MFCs available in the literature. There are many studies dealing with different catalyst but only a few studies can be found in literature dealing with binder materials for ORR in MFCs, and these are presented in the next section.
2.4.2 Binder

Nafion and PTFE are the most commonly used binder materials for immobilizing catalyst and providing mechanical and current supporting functionality in BES.

The studies carried out on binder materials used in MFCs air-cathodes are summarized in Table 2-1, to show how different the binder materials are and the associated properties (hydrophobic or hydrophilic, cationic, anionic or uncharged, with or without functional groups). The low number of materials tested shows that there is a need for more materials to be tested; especially considering the importance a binder plays in the oxygen reduction reaction. Even though the binder will not participate in the catalytic reaction, it plays an important role in providing the three phase contact and allowing the reaction educts (O\textsubscript{2} and H\textsuperscript{+}) to reach the catalytic center which therefore governs the reaction rate.

Cheng et al. (2005) examined Nafion and PTFE and found that Nafion performed better than PTFE in an MFC air-cathode. Mixtures of Nafion and PTFE in different ratios (1:2 and 2:1) have also been tested, resulting in increased power density with the increase of Nafion in the binder mixture (Wang et al., 2010a).

Poly(dimethylsiloxane) PDMS was tested as a binder material and a replacement for PTFE as base material for diffusion layers. The base material should avoid leakage and should allow oxygen diffusion to the catalyst surface (on the solution facing side of the cathode); PDMS is also cheaper than PTFE but still hydrophobic (Zhang et al., 2010). PDMS was also investigated in a later study by Zhang et al. (2012b), deployed as an hydrophobic binder material, which is highly permeable to oxygen and was found to have lower cathode impedance than Nafion, because of the lower diffusion resistance it presented to oxygen (Wang et al., 2010a).
Table 2-1: Different binder materials used in MFC cathode preparation.

<table>
<thead>
<tr>
<th>binder</th>
<th>properties</th>
<th>catalyst used with</th>
<th>Study by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>Hydrophobic backbone and hydrophilic sidechain proton conductive</td>
<td>Pt, CoTMPP</td>
<td>(Cheng et al., 2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/Pt PbO₂</td>
<td>(Wang et al., 2010a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Morris et al., 2007)</td>
</tr>
<tr>
<td>PTFE</td>
<td>hydrophobic</td>
<td>Pt, CoTMPP</td>
<td>(Cheng et al., 2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/Pd Pt PbO₂</td>
<td>(Zhan et al., 2009b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Wang et al., 2010a)</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane) PDMS</td>
<td>hydrophobic</td>
<td>Pt</td>
<td>(Zhang et al., 2012c)</td>
</tr>
<tr>
<td>Poly(sulfone)</td>
<td>hydrophobic</td>
<td>Pt</td>
<td>(Saito et al., 2010)</td>
</tr>
<tr>
<td>Sulfonated polysulfone - S-Radel *</td>
<td>hydrophilic</td>
<td>Pt Pt FePc</td>
<td>(Saito et al., 2010)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Chen et al., 2012a)</td>
</tr>
<tr>
<td>Q-Radel *</td>
<td>hydrophilic, ionic</td>
<td>Pt</td>
<td>(Chen et al., 2012a)</td>
</tr>
<tr>
<td>Fluorinated poly(arylene ethers)</td>
<td>hydrophilic, ionic</td>
<td>Pt</td>
<td>(Chen et al., 2012a)</td>
</tr>
<tr>
<td>Ethylenediamine tetraacetic acid EDTA</td>
<td>hydrophilic</td>
<td>Pt</td>
<td>(Gong et al., 2014)</td>
</tr>
<tr>
<td>Polystyrene poly(ethylene oxide) PS-b-PEO</td>
<td>hydrophobic</td>
<td>Pt</td>
<td>(Saito et al., 2011)</td>
</tr>
<tr>
<td>Poly(bisphenol-A-co-Epichlorohydrin BAEH</td>
<td>Hydrophilic</td>
<td>Pt</td>
<td>(Saito et al., 2011)</td>
</tr>
<tr>
<td>Polytetrafluoro-ethylene-quaternary 1,4-diazabicyclo-[2.2.2]-octane polysulfone QDPSU</td>
<td>hydrophilic</td>
<td>FePc</td>
<td>(Yu et al., 2012)</td>
</tr>
</tbody>
</table>

Sulfonated and non-sulfonated poly(sulfone) have also been tested as catalyst binder. Poly(phenyl sulfon) (Radel®) was used as a base material and the ion exchange capacity was varied by increasing the degree of sulfonation, hence the hydrophobic base was modified to increase the hydrophilicity (Saito et al., 2010). The results have shown that the hydrophilic nature of the binder had an adverse affect on the performance. The highest current was achieved with the unsulfonated polymer binder, followed by Nafion. The charge transfer resistor $R_{CT}$ was found to increase with increasing ion exchange capacity and was at its lowest when the hydrophobic poly(sulfone) was used. The results led to the conclusion, that the sulfonated poly(phenyl sulfon) hindered the proton transfer to the
binder/catalyst surface. Even though the catalytic surface area was smaller with the hydrophobic binder, as this sort of binder will block the catalyst surface and will not allow proton transfer, it was hypothesized that the ionic concentration gradient on the catalyst interface caused by the sulfonated groups decreased the cathode performance.

The non-fluorinated binders S-Radel® and Q-Radel® were also investigated in a study by Chen et al. (2012a) and compared against quaternary ammonium functionalized fluorinated poly(arylene ether) (Q-FPAE) and Nafion. It was found that Q-FPAE resulted in similar current densities and charge transfer resistance to cathodes fabricated with Nafion as a binder. In another study by Saito et al. (2011) different neutral hydrophilic binders were tested, namely polystyrene-b-poly(ethylene oxide) (PS-b-PEO) with varying hydrophilicity. It was found, that increasing the hydrophilicity increased the electrochemical response compared to hydrophobic PS-OH, which is different to the finding published by Saito et al. (2010) mentioned above, where actually the hydrophobic binder resulted in a better performance. Also a cheap hydrophilic neutral binder was tested Poly(bis-phenol-A-co-epichlorohydrin) (BAEH) and compared against Nafion. It was found that cathodes with BAEH binder only initially had a lower power density, but ultimately the power is limited by biofouling, which was not influenced by the binder used. It was shown that a high water uptake due to the hydrophilicity will increase the performance, but cannot prevent biofilm growth. However, the water uptake is believed to increase the oxygen solubility, ion conductivity and surface area for the ORR. An hydrophilic anion exchange ionomer which is significantly cheaper than Nafion was tested by Yu et al. (2012); quaternary 1,4-diazabicyclo-[2.2.2]-octane (DABCO) polysulphone (QDPSU) is hydrophilic (water uptake 46%) and was compared against PTFE and Nafion. The binders were tested with FePc catalyst on a rotating disc electrode as well as in a MFC. QDPSU showed a higher ORR current compared to Nafion, when CVs were measured with oxygen gas. Recently, ethylenediamine tetraacetic acid (EDTA) was tested as a non-polymeric new binder material and compared against Nafion. Different concentrations of EDTA (0.02-0.2 mol l⁻¹ EDTA), have been tested, with the lowest concentration of 0.02 mol l⁻¹ EDTA resulting in a 42% higher power than with Nafion. It was concluded that EDTA transfers protons from the phosphate buffer (H₂PO₄⁻ → HPO₄²⁻) to the catalyst interface (Gong et al., 2014). However, having the protons necessary for the ORR transferred in form of a phosphate-anion might result in lower performance if real wastewater is used instead of buffer.
The summarized results show, that there is no clear agreement on the findings in terms of hydrophilicity and hydrophobicity or if the binder needs to provide proton conductive properties or any ionic structure. Hence further studies are necessary to clarify those points. For this reason chapter 6 presents the application of Ionic liquids (IL) as binder material, which have not been considered yet.

### 2.4.3 Ionic liquids as binder materials

Ionic liquids (IL) are an interesting and relatively new set of substances with several unique properties such as high conductivity, high viscosity, ionic structure and hydrophobicity, very low volatility and high biocompatibility, which makes them interesting candidates for electrode modifications (Opallo and Lesniewski, 2011). For their application as a binder material in MFCs, the ionic liquid of choice should be immiscible with water, ideally non-toxic and should exhibit a high conductivity. ILs exhibit strong electrostatic forces between their ions and the properties can vary enormously as a function of their molecular structure, which makes them applicable in batteries, fuel cells, super-capacitor and solar cells, amongst many other applications (MacFarlane et al., 2014).

In general, properties such as surface tension, viscosity and density, depends mainly on the alkyl chain in the cation and/or steric form and symmetry; whereby others are given mainly by the anion (thermal stability, viscosity and miscibility) (Takeuchi et al., 1987, Malik et al., 2011). Small anions are associated with a diffuse negative charge and less hydrogen bondings resulting in a lower viscosity, whereas long, bulky alkyl-chains result in an increase in viscosity of the organic mixture. Ionic liquids have been used as droplets or a film on the electrode surface, in combination with carbon nanotubes in a gel or in carbon paste electrodes (Opallo and Lesniewski, 2011). In order to act as binder in carbon paste electrodes, ILs need to have the necessary high potential window for their oxidation and reduction, hence for their use as ORR binder, the IL of choice should not undergo a reduction reaction in the MFC potential range. In general the potential windows have been reported to be between 4.5 V and 5.0 V (Fujita et al., 2012). For the common IL - Butyl-3-methyl-imidazolium hexafluorophosphate [BuMeIm]⁺ [PF6]⁻ a potential window of 7.0 V was found (Suarez et al., 1997). Hence ILs have the potential to be implemented but no reports of their use in MFCs has been found. One of their most appropriate uses in MFCs might be as binder material, as presented in chapter 6.
Several ionic liquids have been used as binders in carbon paste electrodes, due to their high viscosity, hydrophobicity and as ILs are composed of charged species, they exhibit ionic conductivity, which can be as high as 14 mS cm\(^{-1}\) for ethylmethylimidazolium \([\text{EtMelm}]^+\) based IL (Galiński et al., 2006). One of the most commonly used ionic liquid in carbon paste electrodes is 1-Butyl-3-methyl-imidazolium hexafluorophosphate \([\text{BuMelm}]^+ [\text{PF6}]\), which exhibits a conductivity of 1.8 mS cm\(^{-1}\) (Fuller et al., 1998) and has been used in the study presented in chapter 6. This ionic liquid has been used in a Nafion/nano-CaCO\(_3\)/Hb film electrode as a H\(_2\)O\(_2\) biosensor (Sun et al., 2007), as well as in an electrode for sensing dopamine (DA), ascorbic acid (AA), and uric acid (UA) (Safavi et al., 2006). The same IL \([\text{BuMelm}]^+ [\text{PF6}]\) was also used in a Glucose Oxidase sensor, in which Multiwall Carbon Nanotubes (MWCNTs)-modified electrodes have been prepared by using this IL as the binder (20 mg CNTs and 0.2 ml IL) (Liu et al., 2007) as well as in combination with single-walled carbon nanotubes (SWCNT) in the ratio 1 mg to 20 µL to detect the pesticide methylparathion (Fan et al., 2008a). Another hydrophobic room temperature ionic liquid (RTIL)-1-decyl-3-methylimidazolum bis(trifluoromethylsulfonylimide) was also used as binder in a ion transfer carbon paste electrode (Shul et al., 2006). Many different ratios of the carbon material and the IL have been tested to guarantee mechanical stability (Opallo and Lesniewski, 2011); however drawbacks reported might be the solubility of the \([\text{PF6}]^-\) anion (Samec et al., 2009) or the high capacitance of IL based carbon paste electrodes.

Protic Ionic liquids have also been tested for their application in fuel cells, because they can accept protons and act as proton carrier (Nakamoto and Watanabe, 2007). It was also reported that the protic IL diethylmethylammonium \([\text{dema}]^+\) and ethylmethylpropylammonium \([\text{empa}]^+\) with bis(trifluromethanesulfonyl)amide \([\text{NfO}]^-\) as the anion, lowers the overpotential for the oxygen reduction reaction in intermediate temperature fuel cells and were furthermore found to be immiscible with water (Yasuda et al., 2009). On the basis of these findings and the additional properties necessary for their application in MFCs (immiscibility with water, liquid at room temperature) \([\text{empa}]^+ [\text{NfO}]^-\) was chosen to be tested as binder in MFCs in the study presented in this thesis. So far, ionic liquids have not been investigated in microbial fuel cell air-cathodes, but several studies presented above show that IL can be used as a binder for the preparation of carbon paste electrodes.
2.5 Microbial fuel cells operated on real wastewater

Apart from the reactor design/configuration and chosen materials there are other intrinsic parameters of the wastewater, which will affect MFC performance. The most important parameters are the wastewater composition (complexity), concentration of organic matter, temperature, pH and conductivity.

The internal resistance lowers the theoretical cell potential from $E^0 = 1.105 \text{ V}$ (16.9 mM acetate as substrate, pH=7 $p_{\text{O}_2} = 20265 \text{ Pa}$; (Logan, 2008)), due to the losses mentioned in section 2.1. The design of the reactor can lower the ohmic resistance by bringing the anode and cathode into close vicinity and by increasing the mixing to decrease the mass transfer losses and avoid local pH gradients near the anode and cathode surface. In contrast, activation losses are more dependent on materials than design and in the case of the anode, the polarization resistance will also be affected by the biofilm (Manohar et al., 2008a) and its maturity (Ramasamy et al., 2008). The pH does not only affect the biofilm but together with the amount of dissolved ions in the waste stream also influences the ohmic resistance of the MFC. Consequently the type of wastewater was found to be a crucial consideration for MFC performance, as low COD content and low conductivity will be detrimental to such performance.

Hence the reactor design and materials can only lower the losses up to a certain degree from which the intrinsic characteristic of the waste will govern the performance. The objectives for implementing MFCs can be to maximize the power and/or to minimize the COD content; the achievement of both is a challenge as one might militate against the other option. If MFCs are used as a polishing stage, to lower COD down to acceptable discharge limits, high turbulence is necessary for mixing in order to keep the mass transfer losses low and lower power can be expected at lower organic loading rates. Kim et al. (2010) have shown that a tubular longitudinal MFC reactor operated with sucrose as substrate at low organic loading rates of 0.04-0.42 g COD l$^{-1}$ d$^{-1}$ under R=150 $\Omega$ can be used as an effluent polishing stage and the power increased with the organic loading.

Waste streams such as domestic wastewater have been used in MFCs but resulted in lower power than synthetic wastes due to their low conductivities (1.80 ± 0.54 mS cm$^{-1}$, pH = 7.3-7.5; (Ahn and Logan, 2010)) and COD concentration. The importance of the solution conductivity was demonstrated by Cheng et al. (2011), who reported a 107% increase in the power density from 16 W m$^{-3}$ at 1.7 mS cm$^{-1}$ to 33 W m$^{-3}$, when the
conductivity was increased to 7.8 mS cm\(^{-1}\). Nam et al. (2010c) have clearly shown the correlation between the ohmic resistance and the conductivity of the feed and have found that the buffer concentration is not defining the power production, but rather it is the feed conductivity. Hence high conductivity waste streams are desirable as reactor design and materials cannot compensate the ohmic losses caused by low solution conductivity.

The more appropriate feedstocks for MFCs exhibit higher COD concentration and conductivity than homogeneous domestic wastewater. Such desirable waste streams may include those from industrial processes such as brewery wastewater (Wen et al., 2010, Feng et al., 2008), starch- (Lu et al., 2009), food- (Heilmann and Logan, 2006) and meat processing wastewaters (Heilmann and Logan, 2006), swine wastewater (Min et al., 2005), distillery wastewater (Mohanakrishna et al., 2010), landfill leachate (Gálvez et al., 2009) as well as effluents form diary (Venkata Mohan et al., 2010). One study by Velasquez-Orta et al. (2011a) compared four different types of wastewater (bakery, brewery, paper and diary) in the same reactor configuration and found significant differences in the bacterial community and high current output was only observed with paper wastewater. Also it was shown that an increase in wastewater conductivity produced an increase in current production irrespective of the type of wastewater used.

The COD content of the waste can only indicate an estimate of the expected performance; better estimations are expected from the soluble COD content. In a study by Velasquez-Orta et al. (2011a) it was concluded that high quantities of poorly degradable compounds may require the use of several processes to achieve effective degradation. It was shown that simple substrates such as acetate resulted in higher current than complex substrates such as starch which needed a fermentation-hydrolysis step before being consumed. Further it was found that the rate of hydrolysis limited the MFC performance as the rate for fermentation was ten times higher (Velasquez-Orta et al., 2011b). Hence, the composition and complexity of the organic materials and their concentrations, especially the content of lower carbohydrates such as VFAs, is crucial in determining the performance. Volatile Fatty Acids (VFAs) were found to be the most suitable substrate for electrogenic bacteria. Above all those mentioned, non-fermentable acetate is most suitable as demonstrated in section 2.5.1.
2. Literature Review

2.5.1 Coulombic efficiency and its dependence on feed complexity

Coulombic Efficiency was found to be strongly dependent on the complexity of the carbon source used. Previous studies have shown that acetate results in higher CEs than fermentable substrates. For example Min and Logan (2004) found this to be the case with acetate CE (65%) exceeding that of fermentable substrates such as starch (21%), dextran (17%) or glucose (14%). The same trend was observed by Chae et al. (2009), who found the highest CE for acetate (72.3%), followed by butyrate (43.0%), propionate (36.0%) and glucose (15.0%). This is also reflected in the energy conversion efficiency (ECE) which was found to be 42% with acetate, but only 3% with glucose (Lee et al., 2008b). The usage of lower carbohydrate such as acetate, propionate and butyrate will cause lower parasitic side reaction activity compared to fermentable substrates.

The most common side reactions which reduce electron harvest from the maximum for a certain substrate are methanogenesis and aerobic activity stemming from dissolved oxygen. However, metal- nitrate- and sulfur reducing bacteria can also lower the CE (He et al., 2005, Logan et al., 2006a). Hence the ideal feedstock for MFCs to achieve high biomass to electrical energy conversion efficiencies is high in VFAs and low in complex organic soluble chemical oxygen demand (sCOD); and should exhibit a relatively high conductivity. For these reasons the integration of MFCs and MECs with anaerobic treatment processes such as Bio-hydrogen and Bio-methane production processes has been proposed to improve the energy recovery and sustainability of the treatment process (Guwy et al., 2011, Pham et al., 2006, Premier et al., 2013a).

2.5.2 Pre-treatment and pre-fermentation of the feedstock

Energy recovery from complex waste streams in form of bio-electricity from MFCs can be enhanced by pre-treating the waste to convert the complex matter into a substrate suitable for electrogens by hydrolysis and other degradation reactions, such as fermentation. Recently, Quan et al. (2014) have investigated different pre-treatment methods for Cassava alcohol wastewater produced from the bioethanol production industry. Solid-liquid separation, ultrasonication and pre-fermentation where applied prior to their usage as MFC substrate, by which the latter was found to be the most effective. Also sludge from different sources (primary sludge, secondary excess sludge, anaerobic digestion sludge) has been used as feed in microbial fuel cells after different pre-
treatment methods were applied, such as thermo-, alkaline-, ultrasonic-, ozonation- and microwave-treatment (Oh et al., 2014, Mohd Yusoff et al., 2013, Xiao et al., 2013). The various pre-treatment methods were applied to increase the amount of soluble COD available and consequently enhanced electricity generation.

Ozonation is also beneficial for the mineralization of organic compounds such as tannin, lignin and gallic acid with adsorption efficiencies up to 100% up to an ozone dose of 2 g adsorbed per gram initial TOC (Saroj et al., 2005) or as a pre- or post-treatment to aerobic treatments, (Saroj et al., 2006). Ozonation was also used to reduce sludge and the soluble biodegradable organics produced were successfully used for improved denitrification and biological phosphorous removal (Saroj et al., 2011).

Anaerobic systems such as anaerobic digestion (AD) and bio-hydrogen (Bio-H$_2$) will generally discharge effluents which are still burdened with relatively high concentrations of organic contaminants. The soluble components of these contaminants include several volatile fatty acids (VFAs), which are odorous and increase biological oxygen demand (BOD) on the receiving environment. Post-processing would be required to remove contaminates and/or realize this energy potential; and would benefit from appropriate technologies (Guwy et al., 2011). The effluent from an hydrogen reactor is especially high in VFAs (in the region of 6000 mg l$^{-1}$ (Premier et al., 2013a)), whereas the total VFA content of a well operated AD reactor will be lower than 200 mg l$^{-1}$, as higher concentrations will inhibit methane production. Furthermore such effluents exhibit high conductivities of more than 10 mS cm$^{-1}$, often due to the addition of regulatory chemicals such as sodium hydroxide.

Goud et al. (2011) found that pre-fermentation of food waste increased the power in MFCs by hydrolysis of the raw substrate into a more utilizable form for electrogens. Also hydrogenic dark fermentation from food processing wastewater (Oh and Logan, 2005) as well as coffee processing wastewaters (Nam et al., 2010a), cane molasses (Pandit et al., 2014) and glycerol (Chookaew et al., 2014) were linked to MFCs. In a two step continuous process the effluent from hydrogen production using food waste was diluted with domestic wastewater and fed to an MFC (Pant et al., 2013). Similar anaerobic hydrogen production with glucose as substrate was continuously operated with an MFC as a second stage to optimize the energy harvested (Sharma and Li, 2010). The combination of MFCs with AD operated on Arthospira maxima biomass was carried out recently (Inglesby and
2. Literature Review

Fisher, 2013). In all these studies the integration of microbial fuel cell with anaerobic pre-treatment was tested as a way to increase the total treatment efficiency and energy conversion efficiency and/or achieve polished effluents. All the pre-treatments can help to increase the energy recovery however, anaerobic processes with biogas production seems to be the most suitable pre-treatment.

Even though the effluents of dark fermentation and anaerobic digestions reactors seems to be in ideal source to further extract energy, there are drawbacks that should be kept in mind. Studies (Sharma and Li, 2010, Nam et al., 2010a, Fradler et al., 2014) have shown that high organic loading rates results in low CE as more substrate will be available for side reactions such as methanogenesis, which can hardly be avoided as the effluent itself contains methanogens. Hence the effluents might need to be further diluted before it is supplied to an MFC, especially if directly used from dark fermentation processes as the effluent is known to be high in COD. Lee et al. (2008a) suggested that post-treatment of the MFC effluent might be required if more complex substrates are used. In order to reach the discharge limit after treatment in an MFC it might be more useful to pre-treat the effluent to make use of all the energy stored in the effluent. Hence the wastewater turnover might require a large quantity of smaller MFCs in series. One promising configuration could be tubular modules with helical anodes to optimize mixing and an air-cathode as presented recently (Michie et al., 2014, Kim et al., 2012c). Ren et al. (2007) have shown that electricity can only be extracted from lignocelluloses once it is converted into monosaccharides, by using a binary culture of C. cellulolyticum and G. sulfurreducents. Hence on the one hand the bacterial community should be high on electrogens to guaranty high CEs and consequently would be low in methanogens, but on the other hand a versatile community is preferred to break down more complex carbohydrates present in many municipal and industrial waste streams. An excellent review of different substrates used in MFC and the adverse impact on the performance if real waste is used was published by Pant et al. (2010b).

The pH value of the Bio-H₂ effluent (pH=5-6) and other real waste streams will probably have to be adjusted if directly feed to the pH sensitive MFC community. Hence consideration must be given to the common lack of buffer capacity of real waste streams so that in long term operation a constant pH-decrease can be observed, which might require pH control in scaled up reactors. The addition of buffering agents is likely to need consideration for pH control, as well as providing an opportunity to increase the
conductivity. A decision will be required on a case by case basis, on if the addition of buffer is reasonable, that is, if the performance increase justifies the additional cost. In general external pH control and buffer addition impose additional costs in real application and should be avoided. The implementation to MFC for large scale treatment of diverse waste streams could be higher operating costs in addition to the pumping costs and costs associated with system control to maintain the pH.

MFCs might be of special interest to industries which are charged for their effluent disposal, which occurs in several countries. The focus therefore lays more with the COD removal than with the power production. The technology could be implemented in a decentralized manner, to remove carbohydrates (COD) for which Companies in UK for example, are burdened with discharge costs according to the Mogden formula. This formula considers the COD content as one of the key cost factors. It should be kept in mind that if MFCs are implemented for effluent polishing purpose, long residence times are required to break down larger particles and non-soluble components, hence filtration with solid disposal could be a complementary process.

### 2.6 Methods and operating strategies to improve the power output from MFCs

Due to the losses explained in paragraph 2.1 the cell potential of MFCs is typically between 0.3 and 0.5 V, which is too low to power typical low power consuming electronic devices such as LEDs (2 V, 10-20 mA), photodiodes (33 mW; 10 mA, 3.3 V) (Diamond et al., 2008), or microprocessors (1.8 W; 270 µA, 2.2 V) (Ibrahim, 2006).

Several approaches have been investigated to increase the power from MFCs, including series and parallel connections, maximum power point tracking, external capacitors and charge pumps as well as the intrinsic capacitance of MFC half cells.

Serially and parallel connected stacks of individual MFC unit cells have been successfully demonstrated (Zhuang and Zhou, 2009, Logan et al., 2006c, Jafary et al., 2013). However, serial connection of modules which are hydraulically joined by conductive substrate flow paths face potential losses due to parasitic current flow (Zhuang and Zhou, 2009), which substantially reduces stack voltages. This was also observed by Kim et al. (2012b), who suggested design criteria for scaling up MFC systems such as just connecting unit cells in series which do not share the anolyte and connect such multi cells in parallel. A further
problem which has been observed in MFCs is voltage reversal, which might occur in MFC stacks if the substrate concentration varies between the cells. Also different anodic reaction rates were suggested as possible reason for the phenomenon of voltage reversal (An and Lee, 2014), which can also deleteriously affect the electrogenic biofilm on the electrode (Oh and Logan, 2007). One possibility to avoid voltage reversal was recently reported, showing that maximum power point tracking controlled MFCs in series stack connection were stable even if operated at different substrate concentrations (Boghani et al., 2014).

Several studies deal with maximum power point tracking systems (MPPT) to increase the power extracted by MFCs (Premier et al., 2011, Woodward et al., 2009, Degrenne et al., 2012). By dynamically controlling the load resistance the MFC can be persistently operated at the maximum instantaneous power and is able to generate more power at higher efficiency due to impedance matching, compared to an un-controlled MFC with static electrical load (Premier et al., 2011). It was also reported that MPPT can be beneficial during start up. Boghani et al. (2013a) reported a reduction in start-up time form 42 to 22 days and Molognoni et al. (2014) reported that the start-up time of MFCs fed with swine wastewater was one month shorter compared to the control without MPPT. Other energy management systems tested with MFCs include different DC/DC converter topologies (Degrenne et al., 2011) and their combination with MPPT (Park and Ren, 2011).

Grondin et al. (2012) used intermittent and periodic connection of the load as an alternative to MPPT operation in order to match internal and external impedance to obtain maximum power transference. In this study the connection and disconnection time were based on the voltage rather than specific open and closed circuit times. Gardel et al., (2012) used duty cycles of open and closed circuit operation in benthic MFCs to increase the power output. It was shown that the current can be increased after switching from open into closed circuit mode without affecting the anodic biofilm community. Furthermore it was suggest, that the diffusion is the limiting factor in delivering power to the circuit, as the mass transport in the anode and cathode surface control the electrochemical reaction.

Storing the energy produced in an external capacitor has also been found to be beneficially. Shewanella oneidensis MR-1 growing on lactate was used to produce power intermittently, by accumulating the energy in a capacitor and then discharging it through a
load (Dewan et al., 2009). The voltage was increased by 111% when an external capacitor was employed and intermittently charged by a MFC compared to continuous electrical operation under fixed load. This study concluded that if the size of the capacitor is selected properly, it can be more efficient than continuous energy harvesting under constant load. Liang et al., (2011) reported a 22-32% higher average current, when the BES first charged a capacitor and then discharged directly through the BES. Kim et al. (2011c) charged four capacitors in parallel to avoid voltage reversal in MFC, and discharged them linked in series, which boosted the voltage up to 2.5 V. By operating the system with a four-minute charging and discharging interval, the peak power reached 2.5 times the maximum power from a MFC. Furthermore the power of an MFC was stored in a capacitor and then used to increase the hydrogen production rates of an MEC which requires a minimum of 800 mV (Hatzell et al., 2013). Ren et al. (2013) investigated the switching time for a MFC-capacitor system and found the highest average current occurred at a switching interval of 100 s.

Another approach to using the capacitance effect was recently presented by Liu et al. (2014b) in which anode particles made of granular activated carbon with a biofilm attached, were fluidized and only intermittently discharged when in contact with the anode current collector. The same concept was used in microbial fluidized electrode electrolysis cell (MFEEC) to enhance hydrogen gas production. The hydrogen gas yield was 116% higher than in the control without granular activated carbon, due to the intermittent contact of the capacitive particles with the anode (Liu et al., 2014a).

Open circuit energy accumulation within an MFC was first observed in sulphate/sulphide mediated MFCs by Ieropoulos et al. (2005), as an initial burst of power was observed when reconnected to a load. Charge accumulating capabilities in discontinuous operation were recently demonstrated for Geobacter sulfurreducens (Schrott et al., 2011) and Shewanella oneidensis (Uría et al., 2011) during open circuit operation. Both strains were found to be capable of direct electron transfer and could store electrons in their extracytoplasmic cytochromes even in the absence of an electron acceptor during open circuit operation. Once a terminal electron acceptor becomes available (electrode under closed circuit operation), the cytochromes are continuously oxidized and release the stored charge. Schrott et al. (2011) have shown that Geobacter biofilms can store the electrons for 25-30 min, whereby the amount of stored charge was controlled by the applied potential. The study which investigated Shewanella oneidensis showed an almost
liner relationship between the disconnection time and the stored charge up to 60 min (Uría et al., 2011). By using this mechanism of charge storage, a single Geobacter cell was estimated to store $10^7$ electrons ($1.60 \times 10^{-12}$ C) (Esteve-Núñez et al., 2008). Recently a study investigated the electrode potentials with respect to the reference electrode during alternating OC/CC operation in small 25 ml reactors and showed that the COD removal rates were higher in CC mode when compared to OC mode (Sevda et al., 2014a).

A pseudo-capacitor, which combined a Geobacter sulfurreducens biofilm with a double layer capacitor on a conductive surface has also been investigated and was found to increase the capacitance by two orders of magnitude (Summers et al., 2010). In this context pseudo-capacitive anodes were also investigated further for their implementation as renewable energy storage in MFC. As the anode potential is less rapidly reduced towards the open circuit potential than in a non-capacitive electrode, it has been proposed that electron transfer and storage of electrons in the capacitive anode during current interruption would be maintained (Deeke et al., 2012). The effect of different capacitive layer thicknesses consisting of activated carbon powder, PVDF solution and N-methyl-2-pyrrolidone (NMP) (0.2 mm, 0.5 mm and 1.5 mm) were also considered (Deeke et al., 2013). Very recently the pseudo-capacitance of a carbon veil modified anode with polypyrrole (PPy)/9,10-anthraquinone-2-sulfonic acid sodium salt (AQS) and RuO$_2$ nanoparticles was determined showing that the charge stored and released is highly dependent on the anode capacitance (Lv et al., 2014) and also polypyrrole-graphene oxide (PPy-GO)-modified graphite felt anodes were tested (Feng et al., 2014) with respect to their charge storage capability. Furthermore the addition of Fe$_3$O$_4$ in an earlier study showed an increase in the anode capacitance of an MFC (Peng et al., 2012) and was found to accelerate the anodic electron transfer (Peng et al., 2013).

Hence several possibilities to enhance the power to a more useful level for practical applications have been proposed including power control strategies using algorithm (MPPT), pseudo-capacitive electrodes, external capacitors, DC/DC converters and more. In this thesis MPPT was used to control a tubular 4 module reactor, see section 3.8.1 (operation mode B), to increase the COD removal rate. In the study presented in chapter 5 the internal capacitance of the 2 module tubular MFC was studied.

There are however, other approaches to increase the power and/or which can extent the application area to make MFCs more attractive to industry. The focus has enlarged from wastewater treatment capability and power production and an increasing emphasis has
been placed on the many other possible applications for BES, which have been shown to be feasible and are probably more economical, as presented in section 2.6.1, which follows.

2.6.1 Integration and combinatory approaches

Recently the trend is towards integrating and combining BES with other systems to make them more versatile. A broader field of application also makes them more economically effective as synergistic effects can increase the performance and lower the payback time.

In this section different approaches to integration and combination are summarized (see Figure 2-4), which should help the understanding of which way MFCs benefit from such integration and what sort of problems may arise when other processes are integrated with MFCs. Many of the integration approaches deal with desalination (of seawater), additional potential from salinity gradient energy (reverse electrodialysis) or the removal/reduction of metal ions. In chapter 7 and 8 an integration of MFC with supported liquid membrane permeation is introduced for zinc removal. Similar to other integration strategies summarized in Figure 2-4, membranes play a key role. In the 3 chamber reactor used in these studies the chambers were separated by a bipolar membrane and the supported liquid membrane, which will be explained in section 2.9. Hence it is important to understand the effect of membranes and their interactions with the adjacent solutions when used in an MFC.
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One approach, which allows desalination in microbial fuel cells is called microbial desalination cell (MDC). Many different systems have been proposed, the simplest one consists of an anion exchange membrane (facing the anode chamber) and a cation exchange membrane (facing the cathode chamber) stack in between the two chambers and salt water in between the two membranes. Desalination is achieved by Cl\(^-\) and Na\(^+\) transfer through the membranes into the adjacent chambers. The driving force of the process is the current production which forces charge balance. A proof of concept study by Cao et al. (2009) revealed the limitations, as the internal resistance increased by 39 times by the time desalination was achieved. A further problems arising from such a design are pH imbalances in the anode and cathode chamber. The transfer of Cl\(^-\) into the anode leads to the formation of HCl and the transfer of Na\(^+\) results in the formation of NaOH as protons are released in the anode and consumed in the cathode, which was not desired. Hence similar to simple MFC configurations, pH gradients near the electrodes which adversely affect the performance were observed. An acid environment next to the anode can harm electrogenic bacteria and an alkaline solution on the cathode side can

Figure 2-4: Overview of integration and combination approaches in MFCs.
easily cause proton limitation. Hence it is especially important to find a process which, when integrated with an MFC, can reverse the problem and can lead to a catholyte high in protons, which can increase the cell potential as discussed in section 2.3. Also, the transfer of other ions (Br\(^-\), SO\(_4^{2-}\), Mg\(^{2+}\), Ca\(^{2+}\)) has been investigated. A possible area of application of such ion transfer is their use as a pre-treatment for Reverse Osmosis (RO) to reduce the losses caused by the internal resistance (Mehanna et al., 2010). Also a bipolar membrane microbial desalination cell was introduced for simultaneous desalination as well as acid (HCl) and base (NaOH) production (Chen et al., 2012b).

Another recent approach deals with the integration of reverse electrodialysis (RED) from entropic energy driven by a salinity gradient. Hence instead of desalinating the water the mixing of high and low concentrated salt water will produce two streams with medium salt concentration. It was shown that a synergistic effect increases the performance/cell potential of a Microbial reverse-electrodialysis cell (MRC) relative to the individual systems. In a proof of concept study by Kim and Logan (2011) an energy efficiency of 42% under 1000 Ω was achieved. Also microbial reverse-electrodialysis chemical-production cells (MRC) were introduced to produce acid and alkali using a bipolar membrane without using external power supply (Zhu et al., 2013). However, in this configuration NaOH is produced on the cathode side, which will lower the ORR potential and lower the additional power from the RED stack.

Apart from the integration approaches introduced above, combinations with other systems were also carried out; one of them is capacitive deionization. Capacitive deionization based electroosorption, was coupled with microbial fuel cells (CDI-MFC) to simultaneously treat wastewater and desalinate low-concentration salt water with a desalination rate of 35.6 mg l\(^{-1}\) h\(^{-1}\) (Yuan et al., 2012). Also different desorption modes (Yuan et al., 2012) and connection styles (series and parallel) (Feng et al., 2013a) were tested to recover the electrostatic energy in a CDI cell. This technology for desalination in MFCs does not require membranes, as in the studies introduced above, but uses capacitance. This shows that the capacitance in an MFC can not only be used to increase the potential (as reviewed in section 2.6), but can also be used to desalinate water. Eom et al. (2011) combined a ferric-based MFC with a ferrous based fuel cell (M2FC), to overcome the depletion and sustainability problem allowing ferrous to be oxidized to ferric in the anode compartment of the FC and to be transformed back in the MFC cathode chamber so that the re-oxidation and oxidation is carried out in a closed process.
This shows that the functionality of BES expanded significantly within the past couple of years and further integration and new applications can be expected considering the increase of published papers in this area observed since 2010. However, there are also some drawbacks such as the lowered conductivity of the electrolytes (desalination) and the higher internal resistance due to the membranes.

Whereas this section focused on integration processes mainly involving functional membranes or osmosis membranes, the next section introduces MFC reactors capable of removing metal ions.

2.7 Metal removal in BES

Current and restrictive legislation along with the intrinsic value of some metal ions make the removal and recovery of such materials from different wastewaters desirable, not only from an ecological but also form an economic point of view. The increasing value of metal resources and the need to remove heavy metal pollutants from water resources make the recovery of metal ions from industrial wastewaters, acid mine drainage and natural leachates an important issue. The EU Water Framework Directive (Commission, 2012) restrict the discharge of toxic metals, nutrients and BOD in wastewater effluents and has led to the need for effective treatment processes capable of removing contaminants (San Roman et al., 2010).

Also domestic waste can contain high levels of both organic matter and metal ions (Liang et al., 2010), which require suitable treatment to achieve regulatory levels of toxic metals and biological oxygen demand (BOD) prior to discharge to the receiving environment.

![Standard redox potentials](image)

Figure 2.5: Standard redox potentials of metals recovered in microbial fuel cell studies.
Common methods to remove metal ions include chemical methods such as precipitation, physical methods such as membrane filtration or ion exchange and biological methods (bioremediation and biosorption). Many processes come with limitations and disadvantages. Precipitation of metals as hydroxides, sulfide or chelation creates large amounts of toxic sludge, biological methods such as biosorption are not selective as they mainly interact with functional groups on the surface of the bacteria. Also ion exchange is not sufficiently selective and has to be exchanged or regenerated when saturated.

Several studies deal with the removal of metal ions in microbial fuel cells, showing that BES having a great potential and might play a key role in the future as an energy efficient process to recover ions of their salts from aqueous solutions and additional treating organic matter while producing power.

Theoretically any redox-couple which shows a higher redox potential than acetate can be an electron acceptor instead of the commonly used air cathode, which reduces oxygen. All the metal ions with a more positive redox potential than acetate can be recovered in microbial fuel cells. However, the recovery via elemental deposition on the cathode is thermodynamically restricted to silver (Ag\(^+\)) and copper (Cu\(^{2+}\)), considering the standard redox potential for acetate (HCO\(_3^-\)/Ac\(^-\)); E\(^\circ\) = -0.29 V (10 mM; pH = 7), which represents typical conditions in an MFC (see in Figure 2-5).

**Recovery in metallic form**

The most common and effective method for the recovery of silver ions from solutions is electrolysis. In an MFC silver ions can be reduced spontaneously, which results in high theoretical cell potential of 0.970 V (Choi and Cui, 2012); but the reduction potential will be lower if the silver ions are dissolved as a complex such as [AgS\(_2\)O\(_3\)]\(^-\). Tao et al. (2012) used a two chamber system with cation exchange membrane and showed that silver ions Ag\(^+\) can be more rapidly removed than silver in a thiosulphate complex Ag(I). Also a very recent study by Lim et al. (2014) deals with the cathodic recovery of silver in a microbial fuel cell with anion exchange membrane, whereby Wang et al. (2013a) used a bipolar membrane to avoid Ag\(^+\) transfer into the anode chamber. If metal ions are recovered in a microbial fuel cell, the choice of membrane which separates anode and cathode chamber will be important as many cation exchange membranes will allow the transfer of cations into the anode chamber.
Copper

The toxic compound copper has been removed in several studies as it is also spontaneously reduced on the cathode. In theory a cell potential of 0.621 V can be achieved \( E_{\text{emf}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = 0.337 \text{ V} - (-0.284 \text{ V}) = 0.621 \text{ V} \). Heijne et al. (2010) removed > 99.88% of the copper ions, but high removal efficiencies (<99%) were only found to occur below starting concentrations of 100 mg Cu\(^{2+}\) l\(^{-1}\) (Wang et al., 2010b). Tao et al. (2011) tested a pilot scale membrane free BES with a reactor volume of 16 l to treat Cu\(^{2+}\) and also observed the deposition of Cu\(_2\)O. The same problem of Cu\(_2\)O formation was also reported by Zhang et al. (2012c) who investigated the copper removal (96.26% within 12 h) from ammonia solution. Even though all these studies were carried out with pure synthetic solution, the deposition of copper in high purity was difficult to achieve, due to the co-deposition of Cu\(_2\)O crystals, showing the difficulties associated with the direct reduction.

Reduction of metal ions

Other metal ions such as Fe\(^{3+}/Fe^{2+}\) (Ter Heijne et al., 2006a), Hg\(^{2+}/Hg^{+}\) (Wang et al., 2011c), Cr\(^{6+}\) to Cr\(^{3+}\) (Wang et al., 2008a) and Cr\(^{6+}\) to Cr\(^{3+}\) in combination with vanadium V\(^{5+}\) (Zhang et al., 2012a) have been reduced in a BES, but haven’t been recovered in their metallic form. Hence the ions were not actively separated from the solution. In the case of chrome and mercury ions the reduction leads to the formation of a less harmful species, as Hg\(^{2+}\) and Cr\(^{6+}\) are considered as highly toxic in low concentrations. In the study by Wang et al. (2011c), Hg (l) was found on the cathode but also as Hg\(^+\) salt (Hg\(_2\)Cl\(_2\)) precipitated at the bottom of the cathode chamber. The reduction of chrome was also reported in a biocathode system by precipitation as Cr(OH)\(_3\) (Tandukar et al., 2009, Huang et al., 2010).

Metal ion removal with external power

Even though Ni\(^{2+}/Ni\) exhibits a more positive standard redox potential than the anode, the difference between anode and cathode is too small considering the overpotentials to drive the reaction (see also Figure 2-5). Hence nickel has been recovered in MEC mode by applying external voltages of 0.5 to 1.1 V and was furthermore affected by the initial pH and Ni\(^{2+}\) starting concentration (Qin et al., 2012). Also a Cu\(^{2+}\) and Ni\(^{2+}\) containing synthetic
wastewater was treated were Cu$^{2+}$ was deposited on the cathode spontaneously and external voltage was applied to recover nickel (Luo et al., 2014).

**Other approaches**

Recently Cu, Zn and Pb from fly ash leachate, were removed (more than 95%) in a bioelectrochemical system (BES), where only Cu was reduced at the cathode of the system and Zn and Pb were removed in a separate electrolysis cell. 98.5% removal of Cu$^{2+}$, 95.4% of Zn$^{2+}$ and 98.1% of Pb$^{2+}$ were achieved (Tao et al., 2013). Another approach was reported by Xue et al. (2013), who operated a microbial fuel cell-zero valent iron (ZVI) hybrid process to remove As(III) form aqueous solutions and a synergistic effect lead to a higher removal rate than in a ZVI process alone.

Furthermore an MFC's cathode was used for cobalt leaching from LiCoO$_2$, which showed that the addition of Cu$^{2+}$ improved the acid utilization efficiency and the cobalt leaching (Liu et al., 2013b). A similar study by Huang et al. (2013) reported a more rapid cobalt leaching in a MEC by applying 0.2 to 1 V, making it a promising process for cobalt recovery and recycling of spent Li-ion batteries. And also a combination of MFC and MEC was presented recently, in which Cu$^{2+}$ is firstly released from particles LiCoO$_2$ on the cathodes of MFC and than reduced on the cathodes of a MEC (Huang et al., 2014).

Lefebvre et al. (2012) reported the treatment of acid mine drainage, which is produced during weathering of metal sulfides in mine wastes, loaded with iron in an MFC. The Fe$^{3+}$ ions were reduced to Fe$^{2+}$ and then precipitated in the cathode chamber. Another approach was reported by Cheng et al. (2007) in which ferros iron from synthetic acid-mine drainage was completely removed through oxidation into insoluble Fe$^{3+}$ in an abiotic anode chamber. Acid main drainage was also used to create iron oxide nano particles in an MFC which can be transformed into goethite and used in pigments, whereby the particle size can be controlled by the pH value, the initial concentration of Fe$^{2+}$ and the current density (Cheng et al., 2011). Another approach is the addition of bacteria such as *Shewanella putrefaciens* CN32 to acidic solution containing Au$^{3+}$, Co$^{2+}$ and Fe$^{3+}$ to achieve energy savings in the electronotation/electrodeposition process (Varia et al., 2013). Positive shifts in reversible potentials of gold were observed and the bacteria influenced the reaction mechanism from deviation of Tafel plots and influence of mass transfer kinetics (Varia et al., 2014). Also the reduction of Pd$^{2+}$ was carried out with *Geobacter*
2. Literature Review

*sulfurreducens* to produce Pd(0) nano-catalysts (Pat-Espadas et al., 2013, Yates et al., 2013).

Most of the studies were conducted with synthetic wastewater so there is a lack of knowledge on the selectivity and consequent purity of the recovered metal from complex solutions.

2.8 Zinc removal from wastewater

Even though several studies have been carried out there are just two studies, which will be addressed below, considering the recovery of zinc ions in a BES (Tao et al., 2013, Modin et al., 2012a), as zinc cannot be spontaneously deposited on an MFCs cathode, due to the very low standard redox potential of $E^0 = -0.76$ V.

In general zinc is one of the most common heavy metal ions in industrial wastewater, as well as being the most abundant heavy metal found in surface and ground waters. It is mainly used in corrosion protection with steel. 14% of the zinc is produced as zinc base alloy to supply the die casting industry. Construction, consumer goods, transport and electrical appliances are considered as the main application areas (association, 2014).

In the study by Tao et al. (2013) Cu, Zn and Pb from fly ash leachate, were removed (more than 95%) in a bioelectrochemical system (BES), where only Cu$^{2+}$ was reduced at the cathode of the system and Zn and Pb were removed in a separate electrolysis cell. One study by Modin et al. (2012b) reported the simultaneous treatment of Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, and Zn$^{2+}$ containing wastewater. Cu$^{2+}$ was spontaneously reduced on the cathode, whereas Pb Cd and Zn required external potentials of 0.34 V, 0.51 V and 1.7 V, respectively. It was not possible to recover the metals selectively and economically. Pb was deposited with small amounts of Cu and Cd was deposited with Pb and Cu. Also very low Coulombic efficiencies of 1.2-5.3% were observed for the metals recovered in MEC mode; Cu deposition resulted in a CE of 77.2%. This shows the problems associated with electrolytic (zinc) recovery, which requires pure solutions. Chapter 7 and 8 in this thesis deal with a three chamber MFC/SLM integration approach, in which zinc was removed from the middle chamber and selectively re-extracted in the strip chamber. It is proposed that after selective re-concentration the zinc can be reduced on an Al-electrode in the strip chamber. The principal of SLM is addressed in section 2.9.
In a study by Gardner et al. (2013) the zinc influent concentration of 16 wastewater treatment plants was determined and was found to be 180 µg l\(^{-1}\), where 23% were in a dissolved state. It was found that some wastewater treatment plants removed more zinc than others. This inconsistency shows the importance of developing new technologies for the removal of heavy metals and especially zinc.

Common techniques for Zn\(^{2+}\) removal from aqueous solutions include precipitation as hydroxide, sulfide or carbonate, removal via ion exchange (Alyüz and Veli, 2009), adsorption (Chen et al., 2011), evaporation or biosorption (Areco and dos Santos Afonso, 2010). However, at very low metal concentrations (< 100 mg l\(^{-1}\)) the treatment becomes ineffective and energy intensive (Mathuriya and Yakhmi, 2014).

Hence new technologies should try especially, to make the recovery of low zinc concentration polluted streams more efficient. This is the reason why a feed/catholyte of 100 mg Zn\(^{2+}\) l\(^{-1}\) was continuously supplied in the experiments presented in chapter 8. Recently Abourached et al. (2014) have reported high Zn and Cd removal efficiencies in a single chamber MFCs, mainly by biosorption and precipitation of sulphides. However, a zinc concentration of 32 mg l\(^{-1}\) resulted in a significant MFC voltage drop of more than 70%. Feng et al. (2013b) studied the effect of copper shock loads in microbial fuel cell and showed that 125 mg l\(^{-1}\) will completely inhibit the electricity production. Also the microbial composition was different and less diverse after recovering from the shock. This shows the importance of removing heavy metal ions before they enter the anode of a microbial fuel cell.

Hence one option for wastewaters containing both heavy metal ions and organic matter is to treat it first in the cathode to remove the toxic components, which may adversely affect the biofilm, before it is pumped into the anode chamber to further treat the organic COD.

As mentioned before, one of the aims presented in chapter 8 is the electrolytic zinc recovery from the strip chambers after re-concentration of the zinc removed from the cathode/feed chamber. In general there are several processes to recover zinc hydrometallurgical. The different industrial process, which vary in the starting zinc ion- and sulphuric acid concentration are presented in the Table 2-2.
2. Literature Review

Table 2-2: Hydrometallurgical process for the production of zinc (Weigel, 1964)

<table>
<thead>
<tr>
<th>ELECTRICAL VARIABLES</th>
<th>Standard process</th>
<th>Tainton process</th>
<th>Magdeburger process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current</strong> (A)</td>
<td>8000</td>
<td>8000</td>
<td>10000</td>
</tr>
<tr>
<td><strong>Current density</strong> (A m⁻²)</td>
<td>325-475</td>
<td>1080</td>
<td>570-730</td>
</tr>
<tr>
<td><strong>Current yield</strong> (%)</td>
<td>90-93</td>
<td>88-93</td>
<td>90</td>
</tr>
<tr>
<td><strong>Potential</strong> (V)</td>
<td>3.7</td>
<td>3.2-3.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ELECTROLYTE</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn²⁺] start (g l⁻¹)</td>
<td>95</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>[H₂SO₄] start (g l⁻¹)</td>
<td>40</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>[Zn²⁺] end (g l⁻¹)</td>
<td>55</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>[H₂SO₄] end (g l⁻¹)</td>
<td>110</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td><strong>energy consumption</strong> kWh</td>
<td>3.32</td>
<td>3.15</td>
<td>3.1</td>
</tr>
</tbody>
</table>

The reduction reaction on the cathode is mainly carried out on aluminum electrodes, whereas the oxidation of water is carried out on Pb electrodes with 0.5-1% Ag.

**Cathode:** \( \text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} \quad E^0 = -0.76 \text{V} \quad \text{Equation 9} \)

**Anode:** \( \text{H}_2\text{O} \rightarrow 2\text{e}^- + 2 \text{H}^+ + 0.5 \text{O}_2 \quad E^0 = +1.23 \text{V} \quad \text{Equation 10} \)

In order to maintain a favourable hydrogen overpotential and obtain high purity levels and energy efficiencies during electro-winning by electrolysis, the recycling of zinc requires an electrolyte solution free of interfering ions. Zinc deposition is very sensitive to small quantities of particular impurities such as As, Sb, Ge, Fe, Cu, Co and Ni ions (Fosnacht and O’Keefe, 1983). Iron concentrations of less than 10 mg l⁻¹ can significantly reduce the current efficiency (Tsakiridis et al., 2010). The electrolysis is carried out with sulphuric acid (see Table 2-2) as SO₄²⁻ ions are inert during the electrolysis as opposed to other acids such as HCl, which can lead to the formation of harmful Cl₂ gas.

To recycle zinc by deposition on a cathode in high purity, a separation step to gain pure solutions might be required before the reduction takes place. Ions other than those targeted can interfere and can be precipitated with the target ions; they can also change the potential at which the reduction occurs. Hence recycling most likely requires a separation step before the actual deposition, not least to increase the energy efficiency of the process. An alternative and low energy technique for the selective Zn²⁺ removal from solutions to have pure aqueous zinc solutions is reactive liquid-liquid extraction (Noll et al., 2010).
2.9 Supported Liquid-Liquid extraction

Supported liquid membrane extraction (SLM) is a liquid-liquid solvent extraction three phase system (aq/org/aq), where extraction and re-extraction occurs simultaneously. The organic phase is immobilized in a porous hydrophobic support with the advantage that it requires significantly lower amounts of the organic phase than common liquid-liquid extraction systems. In general two different types of SLM can be distinguished; flat sheet supported liquid membrane (FSSLM) and hollow fibre supported liquid membrane (HFSLM). Both provide the desired high surface area to volume ratio. Hollow fibre contactors are more widely used at industrial scale, for instance to separate penicillin (Lazarova et al., 2002b).

The organic phase is held by capillary forces in the pores of a hydrophobic porous membrane, allowing the system to function as an efficient membrane based separation technology (Lozano et al., 2011). The porous supports are made of polyethylene (PE), polytetrafluoroethylene (PTFE), polypropylene (PP) or polyvinylidene fluoride (PVDF). Hence the membranes are mainly hydrophobic, which is beneficial for holding the organic phase and rejecting the aqueous phase. SLM extraction can be applied to a wide range of separation tasks including heavy metal ion recovery from industrial wastewaters (Venkateswaran and Palanivelu, 2005), extraction of pharmaceuticals (Lazarova et al., 2002a) or food additives such as lactic acid (Wasewar et al., 2002).

The organic phase consists of an organic solvent, which is insoluble in water and an extractant (carrier, ionophore). Typically, solvents are long-chain hydrocarbons like n-undecane or kerosene as well as more polar solvents such as di-hexyl ether, dioctylphosphate xylene, toluene, hexane, cyclo-hexane, and others (Jönsson, Parhi, 2012). In general the diluents should have high a dielectric constant and low viscosity. An overview of different extractants is given in Figure 2-6.
The interactions between carrier and target ion are realized through functional groups of the extractant (primary-, secondary-, and tertiary-amines, phosphoric-, phosphonic- and phosphinic- acid and ester groups, ketones, etc.) is based on an ion exchange mechanism, donor/acceptor bonding due to electron donor atoms with free electron pairs (local charge distributions) as well as ion-pair interactions such as hydrogen bonding, van der Waals and induction interactions (Sun et al., 2012), which determine the affinity and selectivity towards the target ion. Above all, the pH value can generate selectivity when used together with the steric hindrance given by long alkyl-chains.

In general three different types of extraction mechanism can be distinguished (Parhi, 2012). Extraction by:

- **Ion-pair formation**
- **Compound formation and**
- **Solvation**

Ion-pair formation is the main mechanism for basic amine components. The free base can extract acid from aqueous solution. The metal ion is then extracted by the anion exchange reaction of the amine. Typical extractants are Alamine-304, Aliquat-336 or Amine-336.
The extraction via compound formation can be acidic such as for D₂EHPA, which has been used as a carrier/extractant for zinc in the MFC/SLM integration experiments (see section 3.8.4). Further extractants of the same type are PC-88A, Cyanex 272 or chelating such as LIX84-I, LiX 64N or LIX860.

Solvating extractants include crown ethers which are cyclic polyethers such as tri-octylphosphine oxide TOPO or tri-n-butylphosphate TBP. The solvate is formed between acids or neutral metal complexes.

Recently ionic liquids have raised interest as extracting agent and/or as diluent to replace common organic solvent based extraction system. The solvation is given by ionic interactions such as Coulombic force, Van der Waals force and hydrogen bonding between extraction complexes and ILs (Sun et al., 2013). Due to their low vapor pressure (low volatility), low combustibility and thermal stability they are considered as green replacements for conventional organic solvents. Ionic liquids are composed of an anion
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and a cation, whereby high Coulombic forces constrain the IL constituents, resulting in practically no vapor pressure (Noble and Gin, 2011). This property makes IL especially desirable for immobilization/impregnation in membranes (supported liquid membrane extraction) as membrane instabilities due to the volatility of the solvents (mostly kerosene) can be avoided.

Ionic liquids can be used as solvent and sole extractant as well as in combination with commercially available extractants introduced above, as the extractant dissolved in organic diluents or as a combination of two ILs. Hence in ionic liquid based separation processes, both the extractant and the diluents can be the same, which results in higher loadings as is typical with standard solvent systems.

Ionic liquids exhibit the same interactions which are common in organic solvents (hydrogen bonding, dipole-dipol and Van der Waals interactions) as well as electrostatic attraction and repulsion (Malik et al., 2011). Long alkyl chains on the cation and/or anion can lower and even stop the miscibility with water and in general significantly change the properties of ILs, which is necessary for their application as an extractant. Apart from the immiscibility with water, ILs should be non-toxic, cheap and should not be consumed (fully recoverable) during the extraction process.

Once the target ions have been extracted into the organic phase, the ions can be re-extracted by stripping with an inorganic acid such as H₂SO₄, HNO₃ or HCl. In this thesis the extractant di-ethylhexylphosphoracid D₂EHPA was used as carrier substance dissolved in kerosene or ShellSol-T. Different concentrations of sulphuric acid H₂SO₄ were used as stripping agent. The mechanism of this system is illustrated in Figure 2-7.
The transport mechanism for the target substance through the membrane can occur by diffusion, which is based on a solubility difference between organic and aqueous phase given by the distribution coefficient $D$ of Equation 11.

$$D = \frac{[C_{\text{org}}]}{[C_{\text{aqu}}]} \quad \text{Equation 11}$$

In facilitated and coupled transport (counter or co-transport), the diffusion is combined with a chemical reaction. In coupled transfer the carrier combines with the metal and moves as a complex through the membrane and finally exchanges the metal ion for the charged species (mostly protons). In counter transport the transfer of the metal ion in the feed solution and the counter ions ($H^+$, Na$^+$) is carried out in opposite directions. The extraction of zinc with $D_2$EHPA is based on this principal. Hence the driving force is the difference between the counter ion concentration in the aqueous phases (feed- and strip phases). In co-transport the co-ions are transferred in the same direction as the target ion.

In facilitated coupled counter current transport the carrier couples the flow of two ionic species, Zn$^{2+}$ and H$^+$ as can be seen in Figure 2-7 and Figure 3-12. Zn$^{2+}$ and $D_2$EHPA as

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Figure 2-7: Schematic illustration of metal removal via supported liquid-liquid membrane in facilitated coupled counter current transport with the EFCE standard test system Zn$^{2+}$|$D_2$EHPA|$H^+$. 

<table>
<thead>
<tr>
<th>Feed phase (I)</th>
<th>SLM (II)</th>
<th>Strip phase (III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$</td>
<td>ZnR$_2$</td>
<td>Zn$^{2+}$</td>
</tr>
<tr>
<td>2 H$^+$</td>
<td>H$^+$</td>
<td>Zn$^{2+}$</td>
</tr>
</tbody>
</table>

Liquid-liquid interface (reversible complex formation)

$$Zn^{2+}_{\text{org}} + 1.5 (RH)_{2\text{org}} \leftrightarrow ZnR_2R_{\text{org}} + 2H^+_{\text{org}}$$

$RH = D_2$EHPA (di-Zethylhexyl phosphoric acid)

$2ZnR_2\text{RH}_{\text{org}} \leftrightarrow 2ZnR_2(\text{org}) + (RH)_{2\text{org}}$
extractant (carrier) is the test system of the European Federation of Chemical Engineering (EFCE). The SLM technique is a combination of three simultaneously occurring processes: extraction from the feed phase to the SLM, diffusion through the SLM and re-extraction to the strip phase. Every Zn\(^{2+}\)-ion transferred to the strip chamber leads to the transfer of two protons into the feed chamber in counter current flow.

In general there are several steps (diffusion and chemical reactions) involved:

- Target ion diffusion to the diffusion boundary layer of the feed phase
- Chemical reaction of the carrier and the metal target ion on the feed/membrane interface (I/II)
- Diffusion of the metal-carrier-complex through the liquid membrane to the membrane/stripping phase interface (II/III)
- The metal-carrier-complex is broken down by a chemical reaction with the stripping reagent
- The stripped metal diffuses to the bulk of the stripping phase
- The regenerated carrier diffuses through the membrane back to the feed/membrane interface (I/II)

It is also possible to re-concentrate zinc in the strip chamber. This is, if the concentration gradient of the second couple of species (mainly protons H\(^+\)) is sufficiently large (Baker, 2012). Therefore the driving force for the removal and re-extraction against an outer concentration gradient into the strip phase is the difference in chemical potentials of the counter ions and therefore the proton potential gradient (Kocherginsky et al., 2007). The uphill transport will only stop when the chemical potential of the protons balances the chemical potential difference of another species (Kocherginsky et al., 2007). Hence the pH (which of course depends on proton concentration [H\(^+\)]) plays an important role as it determines the distribution coefficient (see Figure 2-8) on the interfaces I/II and II/III.
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Zn\(^{2+}\)\(_{\text{aq}}\) + 1.5 \((\text{RH})_2\text{org}\) \(\leftrightarrow\) ZnR\(_2\)RH\(_{\text{org}}\) + 2H\(^{+}\)\(_{\text{aq}}\)

Complexation on the interface I/II

Zn\(^{2+}\) transfer against outer concentration gradient

Decreasing driving force \(\rightarrow\) smaller difference in proton concentration (chemical potential \(\mu\))

Figure 2-8: Schematic illustrations of the driving force for metal ion transfer (here with Zn\(^{2+}\) as model ion) induced by different distribution coefficient on the interface I/II and II/III (\(c_{\text{Zn, org.}}/c_{\text{Zn, aqu.}}\)) at different pH values.
The complex formation for the system $\text{Zn}^{2+} | \text{D}_2\text{EHPA} | \text{H}^+$ is described by the following equations (Bart and Rousselle, 1999) (see also Figure 2-7):

$$\text{Zn}^{2+}_{(aq)} + 1.5 \ (\text{RH})_{2(\text{org})} \leftrightarrow \text{ZnR}_2\text{RH} \ _{\text{(org)}} + 2 \ \text{H}^+_{(aq)} \quad \text{Equation 12}$$

$$2 \ \text{ZnR}_2\text{RH} \ _{\text{(org)}} \leftrightarrow 2 \ \text{ZnR}_2\text{RH} \ _{\text{org}} + (\text{RH})_{2(\text{org})} \quad \text{Equation 13}$$

RH stands for the carrier D$_2$EHPA. The distribution coefficient for Zn$^{2+}$ between the organic and aqueous phase is dependent on the pH and is given by

$$D = \frac{c_{\text{org}}}{c_{\text{aq}}_u} = \frac{[\text{ZnR}_2\text{RH} \ _{\text{org}}]}{[\text{Zn}^{2+}]} \quad \text{Equation 14}$$

The equilibrium constant or extraction constant $K_{\text{ex}}$ is therefore given by

$$K_{\text{ex}} = \frac{[\text{ZnR}_2\text{RH} \ _{\text{org}}][\text{H}^+]^2}{[\text{Zn}^{2+}][\text{(RH})_{2(\text{org})}]^{1.5}} \quad \text{Equation 15}$$

By combining Equation 14 and 15, the following logarithmic dependency between distribution coefficient and the pH value is obtained

$$\log D = \log K + 1.5 \log[(\text{RH})_2] + 2 \ast \text{pH} \quad \text{Equation 16}$$

The driving force for mass transport is a potential gradient through the membrane and diffusive layers, described by Fick’s first law:

$$J = -D \frac{dc}{dx} \ V \ast \frac{dc}{dx} = -D \ast A \ast \frac{dc}{dx} \quad \text{Equation 17}$$

The Permeability coefficient $P$ is given by

$$P = \ln \frac{c_{\text{ex}}}{c_{t=0}} \ast \frac{V}{A} \ast \frac{1}{t} \quad \text{Equation 18}$$

Where $V$ the chamber volume and $A$ the projected membrane area; assuming a linear concentration gradient and immediate reaction between carrier and the target ion on the feed/membrane interface (I/II), so the reaction on the interface I/II is diffusion and not reaction limited, as close to the liquid membrane the transfer is limited by diffusion (diffusive boundary layer). Furthermore, two or more different target ions can be separated from each other when they exhibit a different permeability coefficient.

Di-(ethylhexyl)phosphoracid (D$_2$EHPA) has been used in many studies. Bart et al. (1999) studied the effect and interactions of density, viscosity and interfacial tension of the system $\text{Zn}^{2+} | \text{D}_2\text{EHPA} | \text{isododecan}$ and Ata et al. (2004) studied the zinc transfer with
D$_2$EHPA in the presence of other ions such as Na$^+$, Mg$^{2+}$ and Fe$^{2+}$, where only Fe$^{2+}$ was partially co-transported and sodium or magnesium ions were not removed from the feed phase. Recently, D$_2$EHPA, M$_2$EHPA (which results from a decomposition of D$_2$EHPA) and Cyanex 302 were investigated for the separation of Ni$^{2+}$ and Cd$^{2+}$ ions (Peydayesh et al., 2013). Also, the interactions with TBP were studied by Fatmehsari et al. (2009). Another study investigated the recovery of zinc from an industrial sulphate effluent containing Fe, Pb, Cd, Ca, Mg and Co ions. Zn$^{2+}$ was quantitatively and selectively removed with a higher than 98% efficiency (Pereira et al., 2007).

In general supported liquid membrane extraction has been reported as having many advantages compared to common liquid-liquid extraction. Only small quantities of the solvent and carrier are required. The extraction and re- or back-extraction occur simultaneously, hence the carrier is continuously regenerated. Furthermore it offers the possibility to concentrate the target ion uphill if operated in coupled counter current transfer. However, there are some drawbacks such as the membrane instabilities and the membrane itself, which contributes to a higher mass transfer resistance. To increase the mass transfer and the removal rate, thin membranes are used which leads to a higher mass transfer rate through the membrane. Other factors which influence the mass transfer are temperature and therefore viscosity of the organic phase. Ionic liquids as carrier and diluents are very promising as they exhibit a low vapor pressure which can lower the risk of membrane leakage. SLM technology is one of the most efficient membrane separation processes, which is not based on pressure or a voltage difference but is based on a difference of chemical energy (proton concentration gradient). In general SLM is a very promising method with high selectivity, high separation and high enrichment factors, low operation and capital costs, easy to scale up and low energy consumption (Kocherginsky et al., 2007).

Summarizing it can be said that there is a lack of MFC studies on real wastewater in larger reactors, especially regarding effluent polishing capabilities. Also, several studies have shown that pre-fermented waste is ideal due to the high content of VFAs, but the combination with a two stage bio-gas process has not been carried out yet. Several ways to improve the power were introduced and the capacitance of the reactor itself especially might be useful and needs to be further investigated by taking the interactions of the anode and cathode into account.
New binder materials, needs to be tested in combination with catalysts for the ORR as it is not yet clear which properties the ideal binder needs to have. Ionic liquids could be the ideal candidate due to their versatility and their application as binder in various carbon paste electrodes.

Supported liquid membrane permeation is an ideal candidate for integration in an MFC, but has not been considered. The way in which the integration needs to be carried out has to be examined so that zinc and organic matter can be removed simultaneously and ideally, both subsystem profit from the integration. In both processes the pH value and membranes are of importance, as is the needs to match in such a new reactor configuration.
3 Materials and Methods

This chapter presents a detail description of how the common measurements such as pH, conductivity, Gas Chromatography, zinc concentration, Ion chromatography, Coulombic Efficiency and electrochemical measurements such as EIS were carried out. Then this chapter explains the experimental procedure, the materials and methods of all the experiments carried out in chronology with the results chapters. All the materials and methods of the experimental results presented in chapter 4 to 8 are exclusively presented in this chapter.

3.1 pH-value and conductivity

The pH-value was measured with a pH meter purchased from Mettler Toledo FG2/EL2, Mettler Toledo Inc, Columbus, USA and the conductivity with a Mettler Toledo FG3/EL3 conductivity meter (Mettler Toledo Inc, Columbus, USA), throughout. The pH meter was regularly calibrated in accordance with the manufacturer recommendations with pH buffer solution (pH=4.02 and 7.01) from Hannah instruments.

In the MFC/SLM integration experiments (chapter 6 and 8) the pH-value and conductivity were directly measured with the probe in the cathode chamber.

3.2 Gas Chromatography (GC)

Volatile fatty acids (VFAs), were measured with a gas chromatograph using static headspace GC (Perkin Elmer Clarus 500GC) with flame ionization detector (FID) and a “Nukol” free fatty acid phase column (Supelco Ltd, Poole, UK). The carrier gas was nitrogen. Organic compounds produce electrons and ions in the flame and an electrode is located above the flame. A potential is applied at the burner tip and the ion sensitive current produced in this potential field is measured.

The measurement was carried out according to Cruwys et al. (2002) in the concentration range 0-1000 mg l\(^{-1}\) for propionic, iso-butyric, isovaleric and n-valeric acid and 0-5000 mg l\(^{-1}\) for acetic acid. 2 ml of sample were added to 1.0 ml of NaHSO\(_4\) with 100 µl 2-Ethylbutyric
acid as internal standard in a 22.3 ml headspace vial. The vial was crimped closed with a HS PTFE/Butyl Septa (Perkin Elmer) (Cruwys et al., 2002).

The anodic acetate start and end concentrations (after 72 h) in the batch MFC/SLM experiments as well as the VFA concentration presented in section 4.1.2 with washdown water as a fuel, were assayed using the GC according to the above method.

3.3 Ion chromatography (IC)

The ion concentrations in the cathode/feed chamber at the beginning and end of the experiments presented in chapter 7 were measured by using Ion Chromatography (Dionex ICS-3000). IC uses coulombic interaction between the stationary phase of the column and the ions to achieve separation over time. Anion exchange chromatography uses a positively charged column to retain negatively charged ions. The chloride, nitrate, nitrite and phosphate concentration were determined, along with sulphate. The Dionex ion chromatograph was fitted with an Ionpac ICE-AS6 separation column and the detection method was suppressed conductivity. The eluent was a mixture of 1.7 mM sodium bicarbonate (NaHCO$_3$) and 1.8 mM sodium carbonate (Na$_2$CO$_3$). The calibration was carried out for the range between 0-100 mg l$^{-1}$ for each anion.

3.4 Chemical oxygen demand (COD)

Chemical oxygen demand was determined by using HACH COD test kit vials (range: 0-1500 ppm) based on the standard method (Methode 5220, 435 COD HR) introduced by Dobbs and Williams in 1967. A 2 ml sample of solution was added to the HACH test kit vials containing sulphuric acid, mercury sulphate and chromium trioxide. All the organic matter is oxidized, so resulting in a commensurate reduction of dichromate Cr(II)O$_2$- to Cr$^{3+}$, which induces a colour change and allows the calorimetric determination of the COD content at $\lambda$=620 nm (HACH DR 2800 system, Loveland, CO, USA).

To determine the soluble COD content (sCOD), the sample was centrifuged at 12,000 rpm for 3 min prior to the above analysis.
3.5 Zinc concentration

The zinc concentration in samples was measured by ICP-OES (VARIAN, 710-ES). In inductively coupled plasma optical emission spectroscopy, the samples containing the target ions in trace amounts were injected into the instrument. The technique converts the sample into an aerosol before it is directed to the plasma (at approximately 10 000 K). In the plasma the target ions are presented in the atomic and/or ionic form and reach an excited state through collisional excitation. The atomic and ionic species in their excited states may then relax to the ground state, which causes the emission of photonic energy. As every atom has characteristic quantized energy levels (emission at a specific wavelength) the photons enable conclusion on the analyte. Thus the wavelength of the photons can be used to identify the elements from which they originated and the total number of photons is directly proportional to the concentration. The photons emitted are collected by and focused on a monochromator and the wavelength exiting the monochromator is converted into an electrical signal by a photo detector.

Samples were regularly taken from the feed and strip phase (twice a day or at shorter intervals on the first day) to measure the zinc depletion from the feed- and accumulation in the strip phase in experimentation to combine zinc removal with the treatment of organic materials – see chapter 7 and 8.

A voltammetric instrument (PDV), specifically the PDV6000ultra (ModernWater, Cambridge UK) was used to analyze the zinc concentration. This analysis is based on anodic stripping voltammetry (invented by Jaroslav Heyrovsky in 1959) and is used to detect trace elements in aqueous samples. The measuring cell consists of three electrodes; a Ag/AgCl reference electrode, a Pt-counter electrode and a glassy carbon working electrode (WE). On the WE, a reducing potential is applied and when the applied potential exceeds the ionisation potential of the analyte, the ion is reduced and hence electroplated onto the working electrode surface (M”” + ne⁻ → M).

The target metal ions are electroplated onto the WE and subsequently stripped off by scanning over a certain potential range. The current produced is measured and is proportional to the amount of metal being stripped. As the potential at which the metal is stripped off is characteristically specific for each metal, the metals can be identified and quantified at the same time. Plotting the applied potential against the current will result in a voltammogram in which the current peak area/peak height, are proportional to the
3. Materials and Methods

concentration. Peak height/peak area is compared to a known standard solution under the same conditions.

The zinc analysis was carried out according to the application note: Zinc, Cadmium and Lead at Thin Mercury Film (Water). In which a thin Hg film was platted on the WE to increase sensitivity. Only a small amount of sample is required (lower detection limit 0.5 ppb), which is diluted in 10 ml electrolyte plus 10 ml deionised water. The peak potential for zinc lies between -1200 to -900 mV vs. Ag/AgCl.

The zinc concentration of the continuously operated reactors (see chapter 8) were measured with the PDV. In the first set of experiments the membrane was not wiped before the reactor was assembled. The excess organic phase on the outside of the membrane affected the zinc measurement so that no reliable results were achieved (not presented). This problem was solved by wiping the membranes before building them into the reactors.

3.6 Coulombic efficiency

In general the Coulombic efficiency (CE) describes the ratio between the electrons recovered from the substrate in form of electricity compared to the total amount of electrons in the substrate. This will strongly depend on the substrate used. Per mol of acetate, theoretical 8 mol of electrons can be recovered, while other substrates such as sucrose provide 48 e⁻ per mol.

In fed batch mode (MFC/SLM combination experiment – Chapter 7), the CE was calculated based on the measured acetate concentration according to Logan (2008).

\[
CE_{batch} = \frac{MM \int I \, dt}{n_e \cdot \frac{F}{V_{An^+}} \cdot \Delta c} \quad \text{Equation 19}
\]

Were \( MM \) represent the molar mass of the substrate, \( \int I \, dt \) the current integrated over time (charge), \( n_e \) the number of exchanged electrons and \( V_{An^+} \) the anode chamber volume, \( F \) the Faraday constant (96 485.3365 C mol⁻¹) and \( \Delta c \) the difference between starting- and end-concentration of the substrate.

For the continuous flow experiment and more complex substrate the CE was calculated based on COD with the following formula
3. Materials and Methods

\[ CE_{\text{continuous}} = \frac{MM_{O_2} \times I}{F \times 4 + q \times \Delta\text{COD}} \]  

Equation 20

With 32 \text{g mol}^{-1} for the molar mass of oxygen and four electrons per mol of oxygen \( q \) represents the flow rate and \( \Delta\text{COD} \) the difference between the inlet and outlet COD concentration.

3.7 Electrochemical measurements

Electrochemical measurements were carried out using a Potentiostat Solartron SI 1287 and Frequency Response Analyser (FRA) 1252A (both Amatek-Solartron Analytical, Farnborough, UK) connected to a PC as can be seen in Figure 3-1. The PC was equipped with the necessary software (CorrWare®, CorrView®, ZView®, ZPPlot®) for data analyses and equivalent circuit simulations of the recorded impedance plot.

In two electrode mode the counter electrode (CE) and working electrode (WE) are connected to the electrodes of the fuel cell as shown in Figure 3-1. This configuration measures the whole potential drop (including the membrane) and the current between anode and cathode. In three electrode mode, the reference electrode (RE) is not
connected to the CE and is only connected to the Ag/AgCl reference electrode. A potential can be applied between the WE and RE and the current is measured between WE and CE.

3.7.1 Power curves

The power curves were measured by the potentiostatic method in two electrode mode. A potentiostat 1287 SI (Amatek-Solartron Analytical, Farnborough, UK) was used to apply an external constant potential between anode and cathode after a stable current was measured (10 min). The open circuit potential represents the value after 2 h.

3.7.2 Cyclic voltammetry

Cyclic Voltammetry (CV) measures the current response between WE and CE. A potential is applied with a certain scan rate. The voltage is scanned at a fixed rate and a forward and reverse scan is recorded. A CV gives indications on the reversibility of a chemical reaction and the current correlates with the analyte concentration. For a reversible reaction the position of the peak current is independent from the scan rate. Also the oxidation and reduction peak are separated by 59 mV/number of exchanged electrons and the oxidation peak height equals the reduction peak height.

The CVs presented in section 6.1 were measured at three different scan rates (5 mV s\(^{-1}\), 20 mV s\(^{-1}\) and 50 mV s\(^{-1}\)).

3.7.3 Linear Sweep Voltammetry

Linear sweep voltammetry was used to characterize different cathodic binder and catalyst materials (see chapter 6). A potential range is given and the scanned from the lower to the upper limit. The current response is plotted as a function of the applied potential. The potential was applied between the WE (different electrodes) versus a Ag/AgCl reference electrode. A Pt wire was used as CE and the scan rate was 1 mV s\(^{-1}\).
3.7.4 Impedance spectroscopy

According to Ohms law the resistance is independent of the frequency and the AC current and voltage signals are in phase with each other. Impedance also includes Ohmic resistance, the ability of a circuit to resist the flow of electrical current, but impedance is in general frequency dependent. The electrochemical impedance is measured by applying an AC potential to the MFC and measuring the current through the cell. A sinusoidal potential is applied and the response to this potential is an AC sinusoidal current signal (or vice versa).

The excitation signal can be expressed as a function of time:

\[ E_t = E_0 \sin(2\pi ft) = E_0 \sin(\omega t) \]  

\( E_t \) is the applied potential at time \( t \)
\( E_0 \) the potential amplitude
\( \omega \) angular frequency

For typical impedance measurements, a small excitation signal is used, so that the cell is considered as a pseudo-linear system. In this condition, a sinusoidal potential input to the system leads to a sinusoidal current output at the same frequency. Therefore, the output current signal has a different amplitude \( I_0 \) and is shifted in phase by \( \phi \).

\[ I_t = I_0 \sin(\omega t + \phi) \]  

\( I_t \) output current signal
\( I_0 \) amplitude of the signal
\( \omega \) angular frequency
\( \phi \) phase-shift

The impedance of the system is calculated as:

\[ Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \]  

Where \( Z_0 \) is the magnitude

The impedance can be described as a complex function. The excitation potential input is described as:

\[ E_t = E_0 \exp(j\omega t) \]  

And the resulting current output as:
\[ I_t = I_0 \exp[j(\omega t - \phi)] \]  

Equation 25

Thus, the impedance can be expressed as a complex number:

\[ Z(\omega) = Z_0 \exp(j\phi) = Z_0 (\cos \phi + j \sin \phi) \]  

Equation 26

The expression for \( Z(\omega) \) is composed of a real and an imaginary part. The results of the impedance measurement can be presented as a Nyquist plot or as Bode plot.

Nyquist plots express the impedance with a real part plotted on the X-axis and an imaginary part plotted on the Y-axis (that is negative) as an Argand diagram, with the magnitude and phase angle plotted as a polar plot and the locus of the vectors for a first order equivalent circuit represented as a semi-circle. Each point on the complex plane plot represents the impedance at a certain frequency. The vector of length \( |Z| \) is the magnitude of the impedance and the angle between this vector and the real axis is a phase shift, \( \phi \). The Nyquist plot doesn’t show the frequency at which a specific impedance point is recorded in the plot. In the Bode plot, the X-axis is the logarithmic frequency (\( \log \omega \)) and the Y-axis is magnitude of the impedance (\( \log |Z| \)) or the phase shift \( \phi \).

The EIS data are commonly analysed by fitting to an equivalent electrical circuit model.

### 3.8 Experiments

#### 3.8.1 Four-module tubular MFC on real wastewater

![Carbon veil electrode in four-module tubular reactor.](image)

Figure 3-2: Carbon veil electrode in four-module tubular reactor.

The tubular longitudinal MFC reactor was made from polypropylene tube (230 mm long; 40 mm diameter) and was constructed using a MEA cathode and a spirally rolled carbon veil anode as previously reported (Kim et al., 2010). The anode was fabricated by rolling
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Carbon veil (230 x 450 mm; PRF Composite Materials; Dorset, UK) around a central perspex cylinder of 10 mm diameter. The cathode membrane assembly consisted of a cation exchange membrane (122 x 192 mm; CMI-7000, Membrane International Inc., NJ, USA) assembled with a carbon cloth cathode (163 x 82 mm) containing 0.5 mg cm\(^{-2}\) Pt. The MEA was placed onto the inner anode tube and fixed with a similar perforated plastic tube (Kim et al., 2010). The reactor was inoculated with anaerobic digester sludge (1:10), 40 mM acetate in a 50 mM phosphate buffer, vitamins and minerals (the composition can be found in table 12-1) (\(\chi=9\) mS cm\(^{-1}\)) and enriched under a 1 k\(\Omega\) external load.

The reactor consists of four-modules (each module of 0.25 l), which were separated by ballast and orifice plates to maintain a degree of compartmentalization in the tubular MFC (see Figure 3-2). After batch start-up, the MFC reactor was inclined (30°) and operated continuously.

![Figure 3-3: Schematic illustration of the 3-stage integration of Bio-H\(_2\), Bio-CH\(_4\) and Bio-electricity.](image)

3.8.1.1 Washdown water characteristic and operation

The washdown water investigated was treated aerobically through a dissolved air flotation unit (DAF). The remaining organic content included a relatively high soluble component including volatile fatty acids (VFAs) such as acetic acid (333 mg l\(^{-1}\)) and propionic acid (172 mg l\(^{-1}\)), which represents a favorable substrate for electrogenic bacteria (see Table 3-1). The effluent’s conductivity of 975 \(\mu\)S cm\(^{-1}\) was in the range of domestic wastewater.
Table 3-1: Effluent composition washdown water.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.89</td>
</tr>
<tr>
<td>conductivity</td>
<td>975</td>
</tr>
<tr>
<td>COD</td>
<td>1808</td>
</tr>
<tr>
<td>sCOD</td>
<td>1140</td>
</tr>
<tr>
<td>VFAs Acetate</td>
<td>333</td>
</tr>
<tr>
<td>VFAs Propionate</td>
<td>172</td>
</tr>
</tbody>
</table>

Two different operating modes were testes (mode A and mode B), which differed in the amount of phosphate buffer added to the washdown effluent and the method used to control the systems power output, namely static load vs maximum power point tracking (MPPT).

Figure 3-4: Schematic illustration of the experimental set-up in operation mode A (3 HRTs) and operation mode B (MPPT controlled).

**Operating mode A**

The pH-value was adjusted with 35 mM phosphate buffered saline (PBS; 15 mM Na₂HPO₄, 10 mM NaH₂PO₄). The buffer addition adjusted the pH to 6.8 and the conductivity consequently increased from 975 to 3700 µS cm⁻¹. The effluent was pumped through the four-module tubular reactor and in total 3 l of the washdown effluent were continuously pumped through the reactor (hydraulic retention time (HRT)=24 h, flow rate=0.69 ml min⁻¹, OLR=2.79 g sCOD l⁻¹ d⁻¹); samples were taken after the 3rd HRT. During operation, the influent and effluent were stored in a refrigerator and the effluent from the MFC system...
was subsequently used as influent for the next cycle. This operational mode was adopted to give an indication of the number of in-line modules required to significantly reduce the COD from the waste stream. Each MFC module was connected independently to a static load (R=100 Ω), selected on the basis of prior experience.

**Operation mode B**

In contrast to mode A, separate influent and effluent bottles were not used, but a single chamber was used instead to limit the effect of the excess volume in the recycle line. The flow rate was adjusted so that each cycle represented an HRT of 24 h. Hence steady state conditions were neglected to minimize losses in terms of non-electrogenic substrate degradation over two days, during which the effluent remained untreated in mode A. Also the buffer concentration was increased to 50 mM PBS buffer compared to mode A (35 mM PBS), which resulted in a pH of 6.86 and a conductivity of 7.45 mS cm⁻¹. During operation, the pH was adjusted twice after cycles 3 and 6 by adding 50 mM buffer to avoid pH values dropping below 6, as such low pH would adversely affect the MFC performance. Furthermore, this mode was operated with maximum power point tracking (MPPT) control (Premier et al., 2011); a system control strategy which enables the individual operation of each module at the maximum power point in order to enhance COD reduction as well as the power production.

Two samples of the original wastewater with 50 mM buffer were set aside as controls and kept in the fridge (CF) as well as at ambient/room temperature (CRT); see appendix table 12.3.

### 3.8.1.2 Analysis

A *pseudo* half saturation constant $K_s$ was calculated by fitting Monod-like kinetics (using SigmaPlot™ 12.5) to the plot of sCOD concentration $S$ vs average current $I$ in the four modules, according to $I=I_{max} \frac{(S/K_s + S)}{1}$. The fit from which $K_s$ was determined was shown to have 95% confidence and $R^2 = 0.92$.

The *energy production per COD consumed* ($E_{COD}$ Wh g sCOD⁻¹ consumed) was calculated for each organic loading rate. The basis for the calculation was the measured COD consumption and MFC potential measured after 100 h (3 HRTs), between influent and effluent (end of 4th module).
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\[ E_{COD} = \frac{\sum_{i=1}^{4} \int_{t}^{t+4h} E_{MFC_i} \times I_i \, dt}{\Delta COD \times V_{reac.}} \]  
\[ \text{Equation 27} \]

Where \( E_{MFC} \) is the observed MFC potential (V) after three retention times, \( I \) is the current (A) integrated over one retention time \( t \) (8.3 h) and the four modules, \( i=1 \) to \( 4 \); \( V_{reac} \) represents the whole reactor volume (1 l) and \( \Delta COD \) is the difference between the influent and the effluent (4th module).

The recovered energy from MFC modules (\( E_R \)) over the entire reactor lengths was calculated by using the voltage \( E_{MFCmax} \) and current \( I_{max} \) at the maximum power production, determined from the polarisation curves.

\[ E_R = \frac{\sum_{i=1}^{4} \int_{t}^{t+4h} E_{MFC_i} \times I_i \, dt}{V_{reac.}} \]  
\[ \text{Equation 28} \]

The energy conversion efficiency (ECE) was calculated on the basis of the total influent energy content (\( ECE_{total \, COD} \)) and on the basis of the energy content of the consumed COD (\( ECE_{\Delta COD} \)). The published heat of combustion values for wastewater varies over a broad range of 13.89 to 28.7 MJ kgCOD\(^{-1}\), due to different compositions and measurement methods (Owen, 1982, Heidrich et al., 2010, Shizas and Bagley, 2004). Therefore the energy conversion efficiencies (\( ECE_{total \, COD}, ECE_{\Delta COD} \)) were estimated using two values which represented plausible upper and low estimation limits; \( a = 13.89 \, \text{MJ kgCOD}^{-1} \) (Owen, 1982) and \( a = 23.25 \, \text{MJ kgCOD}^{-1} \). The latter represent the average of two heat of combustion values for different wastewasters after having been freeze dried, calculated using the COD, as reported by (Heidrich et al., 2010).

\[ ECE_{total \, COD} = \frac{E_R}{E_{Inf.}} = \frac{\sum_{i=1}^{4} \int_{t}^{t+4h} E_{MFC_i} \times I_i \, dt}{a \times COD_{Inf.}} \times 100 \]  
\[ \text{Equation 29} \]

\[ ECE_{\Delta COD} = \frac{E_R}{E_{\Delta COD}} = \frac{\sum_{i=1}^{4} \int_{t}^{t+4h} E_{MFC_i} \times I_i \, dt}{a \times \Delta COD} \times 100 \]  
\[ \text{Equation 30} \]
The *Mogden formula* was used to calculate the cost savings with the standard tariffs from Welsh Water for 2013 (WelshWater, 2013):

\[
C = R + V + V_b + B \frac{O_t}{O_s} + S \frac{S_t}{S_s}
\]

Equation 31

- \( R \): sewerage costs \( \text{m}^3 \)
- \( V \): primary settlement treatment costs \( \text{m}^3 \)
- \( V_b \): secondary volume-related treatment costs \( \text{m}^3 \)
- \( B \): secondary strength-related treatment costs \( \text{m}^3 \)
- \( O_t \): settled COD of the effluent in \( \text{mg l}^{-1} \)
- \( O_s \): settled COD of domestic sewage – 500 \( \text{mg l}^{-1} \)
- \( S \): sludge treatment costs \( \text{m}^3 \)
- \( S_t \): suspended solids of the effluent in \( \text{mg l}^{-1} \)
- \( S_s \): suspended solids in domestic sewage – 350 \( \text{mg l}^{-1} \)

### 3.8.1.3 Impedance measurement to investigate the internal resistance of a tubular reactor

Electrochemical impedance spectroscopy (EIS) is a powerful tool for the in depth analysis of MFC, but it also carries the risk of drawing false conclusions, as a large number of different equivalent circuits can fit the measured data. Hence the different circuit elements (\( R_s \), CPE, \( R_{\text{OHM}} \), Warburg diffusion, ...) should be meaningfully attributed to the system components. In this study the main focus was the determination of the internal resistance with increasing number of modules operated in parallel, in order to find the optimum reactor length, as the hydraulic connection between the modules would result in losses. Furthermore, EIS was used to distinguish between the anodic and cathodic activation losses (charge transfer resistance \( R_p \) and double layer capacitance \( C_{\text{DL}} \)).

For this EIS experiments, an improved reactor design was used (Boghani, 2014). The reactor presented in Figure 3-6 consists of an air cathode and a spiral anode with carbon cloth as anode material.

![Figure 3-5: Tubular reactor with spiral anodes and air-cathode (Boghani, 2014).](image)
Impedance spectroscopy was carried out in four different modes as can be seen in Figure 3-6 to determine the internal resistance and the composition in terms of charge transfer resistance, double layer capacitance and ohmic resistance. The internal resistance was determined in the two electrode mode.

3.8.2 Ionic liquids as binder for air cathodes in MFCS

Experimentation was conducted to investigate the use of different binder materials based on ionic liquids, to determine if MFC performance could be so improved. The binders were used in combination with two common catalysts (Pt and Iron phthalocyanine-FePc) for the oxygen reduction reaction. Carbon paste electrodes were prepared with carbon black as the base material on carbon paper electrodes (Fuel cell earth, Wakefield).

Two different ionic liquids were tested and compared to the commonly used binder Nafion® 117 solution (Sigma Aldrich) and PTFE (Polytetrafluoroethylene preparation, 60wt% dispersion in H₂O; Sigma Aldrich). One of the ionic liquids tested was 1-Buthyl-3-methylimidazolium hexafluorophosphate [BuMeIm]⁺ [PF6]⁻ (Sigma Aldrich) a conductive IL,
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as well as ethylmethylpropylammonium nano fluoromethanesulfonate \([\text{empa}]^+ [\text{NfO}]^-\) (io-li-tec Ionic Liquids Technologies Gmbh, Heilbronn, Germany), a proton-conductive IL.

Nafion with PTFE backbone

\([\text{BuMelm}]^+ [\text{PF6}]^-\)

\([\text{empa}]^+ [\text{NfO}]^-\)

Table 3-2: Carbon paste electrode preparation matrix; the paste was applied on carbon paper electrodes with \(A=9 \text{ cm}^2\).

<table>
<thead>
<tr>
<th>binder</th>
<th>Pt: 0.5 mg cm(^{-2})</th>
<th>catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Nafion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40% Pt Vulcano (mg)</td>
<td>11.3</td>
<td>40wt% FePc (mg)</td>
</tr>
<tr>
<td>Carbon black (mg)</td>
<td>33.8</td>
<td>Carbon black (mg)</td>
</tr>
<tr>
<td>H(_2)O (µl)</td>
<td>37.2</td>
<td>Nafion (5%) (µl)</td>
</tr>
<tr>
<td>Nafion (5%) (µl)</td>
<td>300.0</td>
<td></td>
</tr>
<tr>
<td>2% PTFE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40% Pt Vulcano (mg)</td>
<td>11.3</td>
<td>40wt% FePc (mg)</td>
</tr>
<tr>
<td>Carbon black (mg)</td>
<td>33.8</td>
<td>Carbon black (mg)</td>
</tr>
<tr>
<td>H(_2)O (µl)</td>
<td>37.2</td>
<td>PTFE (2%) (µl)</td>
</tr>
<tr>
<td>PTFE (2%) (µl)</td>
<td>300.0</td>
<td></td>
</tr>
<tr>
<td>([\text{BuMelm}]^+ [\text{PF6}]^-)</td>
<td>120 and 180</td>
<td></td>
</tr>
<tr>
<td>([\text{empa}]^+ [\text{NfO}]^-) (µl)</td>
<td>120 and 180</td>
<td></td>
</tr>
</tbody>
</table>

Two different catalyst loadings were tested. Platinum (40% Pt on VulcanXC 72; Premetek, USA) with a loading of 0.5 mg cm\(^{-1}\) and Iron(II)phthalocyanine (Sigma Aldrich) was used with 2 mg cm\(^{-2}\). FePC was mixed with carbon black to give a mixture of 40wt% and ball milled for an hour before being used in the electrode paste preparation. The PTFE solution...
was further diluted with dionized water to give a 2% PTFE solution, which was ultrasonicated before use.

The PTFE binder proportions in the case of the carbon paper electrodes with 0.5 mg cm\(^{-2}\) Pt were chosen as reported by (Middaug, 2006). The paste was applied with a spatula on the carbon paper and then left to air dry overnight.

Additional Activated carbon (Norit, SXRO PLUS, Amersfoort, Netherlands) in combination with different binders has been tested with heat treatment to increase the activity. AC (80 g) were mixed in a mortar, then mixed with the ILs (150 µl) and applied on the carbon paper electrode. The electrodes were either dried on air or at 110 °C for 15 h, before electrochemical measurements were carried out. During the measurements it was found that the paste is not stable when carrying out the measurements, so the activated carbon was mixed with carbon black (see Table 3-3).

### Table 3-3 Composition of activated carbon/carbon black paste electrodes

<table>
<thead>
<tr>
<th></th>
<th>AC (mg)</th>
<th>CB (mg)</th>
<th>Nafion (µl)</th>
<th>[BMIm]+ [PF6]- (µl)</th>
<th>[empa]+ [NfO]- (µl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>30</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>30</td>
<td>200</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>30</td>
<td>200</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>-</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>20</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>30</td>
<td>-</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

The electrochemical measurements Linear Sweep Voltammetry (LSV; scan rate = 1 mV s\(^{-1}\)) and Cyclic Voltammetry (CV; scan rate = 5, 20 and 50 mV s\(^{-1}\)) were carried out in 3 electrode mode. With a Pt coated titanium mesh as CE and a 3 M Ag/AgCl-RE. An air-pump was used to supply oxygen and the measurements were carried out under constant mixing conditions using a magnetic stirrer, as can be seen in Figure 3-8. A commercial 10% Pt electrode was used as control.
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3.8.3 The effect of internal capacitance in a tubular MFC

3.8.3.1 MFC configuration and operation

The experiments to investigate internal capacitance were carried out in two module longitudinal MFC reactors made from polypropylene tube (230 mm long; 40 mm diameter), consisting of a carbon veil anode and air-cathode. A perspex cylinder of 10 mm diameter was used as a former for the anode, around which the carbon veil was rolled (230 x 450 mm; PRF Composite Materials; Dorset, UK), giving a projected surface area of 13 cm$^2$ for the anode and 1035 cm$^2$ for the sheet of veil applied. The air-cathode consisted of carbon cloth (163 x 82 mm; BASF, BIB, Somerset, USA) with a catalyst loading of 0.5 mg cm$^{-2}$ on the solution facing side. The cathode was attached to a cation exchange membrane forming a cathode-membrane-assembly (122 x 192 mm; CMI-7000, Membrane International Inc., NJ, USA). The MEA was placed onto the inner anode tube, with an anode chamber volume of 220 ml and fixed with a similar perforated plastic tube (Kim et al., 2009). The tubular modules were inoculated with anaerobic digester sludge (1:10), 40 mM acetate in a 50 mM phosphate buffer, vitamins and minerals ($\chi = 9$ mS cm$^{-1}$) and enriched under a 1 k$\Omega$ external load. All the results present the averaged value from
duplicate (or higher replicate) measurements as all experiments were carried out simultaneously in two MFC modules.

Figure 3-9 Tubular 2-module MFCs used in the experiment

3.8.3.2 Charging-discharging experiments with different external loads

Four different loads (100, 500, 1 kΩ and 3 kΩ) were chosen to investigate the influence of the load on the internal capacitance in terms of charge accumulation during open circuit and discharge when connected to the load (discharge). Once a stable biofilm had been developed on the carbon veil anode, charge-discharge experiments were conducted under the different resistive loads. Prior to each experiment the anolyte containing the acetate feed was replaced and the charge-discharge experiments were started once a stable voltage was observed (usually the voltage was stabilized overnight). The reactors were manually disconnected from the resistor (OC) to interrupted current production in CC. Seven different OC-periods were investigated (1, 2, 5, 10, 20, 60 and 120 min) and the corresponding voltage response was recorded until stabilization was observed for at least 15 min (completed discharge). Data were recorded every 5 s using virtual instrumentation coded in LabVIEW™.

3.8.3.3 Automated discontinuous operating mode

To investigate the capacitive behaviour during short open and closed cycles, an automated switching system was implemented using a virtual instrument again developed in LabVIEW™ (National Instruments, Newbury, UK) connected through an opto-diode to enable accurate short period switching. These experiments were carried out under R=100 Ω, which matched the internal resistance of the MFC, according to the power curve
measurements. The media (40 mM acetate in phosphate buffer) was replaced and the reactors were left under the static load until steady state current was achieved. The experiments were carried out in a reactor with a mature biofilm, 5 months after inoculation. The data presented herein represent cycles recorded 10 to 20 min after a new cycle (OC/CC combination) was tested. Data were recorded every 0.2 s via the LabVIEW™ base data logger. The potentials between the electrodes and the reference electrode were monitored using the data logger with a multi-purpose Input-Output card (National Instruments, Newbury, UK).

3.8.3.4 Analyses and calculations

The additional energy ($E_{On/Off}$) and additional charge (C) are the values above the steady state values observed under fixed external load, measured under the same condition. These values were compared to steady state voltage ($U_{ss}$), current ($I_{ss}$), energy ($E_{ss}$) and power ($P_{ss}$) under different static loads. The additional charge was compared to the steady state values over the CC period ($t_1$→$t_2$; see Figure 3-10.), with steady state energy, $E_{ss} = \int P_{ss} \, dt$, steady state power, $P_{ss} = (U_{ss}^2/R)$ and steady state charge, $C_{ss} = \int I_{ss} \, dt$.

Figure 3-10: Tubular MFC OC/CC cycling. The additional energy obtained during OC/CC operation is represented by the peak area as compared to power production in static operating condition (steady state operation without On/Off of circuit under a static external load).
Average current ($i_{avg}$) and power ($p_{avg}$) were calculated over the CC time ($t_1 \rightarrow t_2$), as well as over the entire OC/CC cycle ($t_1 \rightarrow t_3$) (see Figure 3-10.), when the automated switching mode was applied.

\[
i_{avg} = \left( \frac{\int_{t_1}^{t_2 \text{ or } t_3} I \, dt}{t_2 \text{ or } t_3 - t_1} \right)
\]

Equation 32

\[
p_{avg} = \left( \frac{\int_{t_1}^{t_2 \text{ or } t_3} I \times V \, dt}{t_2 \text{ or } t_3 - t_1} \right)
\]

Equation 33

To compare the energy generated by the automated switching mode (duty cycling) with the energy generated under a constant load (100 Ω) the parameter “switched mode energy efficiency” (SMEE) was introduced. Hence SMEE represents the ratio between the energy produced during one cycle (closed circuit; $t_1 \rightarrow t_2$) and the steady state energy ($E_{SS}$) under constant load over a time equivalent to the closed and open circuit period ($t_1 \rightarrow t_3$).

\[
\text{SMEE (\%)} = \frac{E_{ON/OFF}}{E_{SS}} = \frac{\int_{t_1}^{t_2} V \times I \, dt}{\int_{t_1}^{t_3} V_{SS} \times I_{SS} \, dt} \times 100
\]

Equation 34

A 3 M Ag/AgCl reference electrode (BASI, Warwickshire, UK) was placed in close proximity to the anode electrode surface, in order to distinguish between anode and cathode potentials.

3.8.3.5 Impedance measurement

In order to investigate the capacitive behaviour of the anode, EIS spectra were measured. The anode was poised at different potentials (-0.5 (OCP), -0.45, -0.4, -0.3, -0.2, -0.1, 0.0, +0.1, +0.2 V vs Ag/AgCl reference electrode) and spectra were recorded over a frequency range of 0.01-300,000 Hz and an AC amplitude of 10 mV. To achieve stable and consistent results, the anode potential was applied for 15 min using the potentiostatic method. The data were fitted to the equivalent circuit presented in Figure 3-11, proposed by (Dominguez-Benetton et al., 2012) using complex non-linear fitting (ZView™ software; from Solartron Analytical Farnborough UK).
3. Materials and Methods

Figure 3-11: Equivalent circuit model of the anode employed to fit spectra, which includes two CPEs to represent the capacitance of the biofilm (CPE\textsubscript{biofilm}) and the Helmholtz layer (CPE\textsubscript{HL}) in parallel with the biofilm resistance (R\textsubscript{biofilm}) and the charge transfer or polarisation resistance (R\textsubscript{CT/P}). A short circuit Warburg diffusion element (WDE) represents mass transfer limitations.

The observed two time constants were attributed to the biofilm and the anode electrode; R\textsubscript{Ω} represents the ohmic resistance between anode and the Ag/AgCl reference electrode and two constant phase elements (CPE) were used to represent i) the double layer capacitance Q of the biofilm and ii) the Helmholtz layer capacitance. The two CPEs were connected in parallel to the respective biofilm (R\textsubscript{biofilm}) and charge transfer or polari\textsubscript{zation} (R\textsubscript{CT/P}) resistances (see Figure 3-11). Whenever semicircle depression is observed the capacitance is replaced by CPEs to fit charge distribution caused by inhomogeneity on the anode surface and spatial differences in the biofilm activity. Diffusion limitations were considered by using a Warburg diffusion element (WDE). Hsu and Mansfeld (2001) presented a formula which was adopted here; C\textsubscript{HM} = Q.w\textsubscript{max}\textsuperscript{α-1}(F) was used to correct the Q values from fitting the CPE (F s\textsuperscript{α-1}), where w\textsubscript{max} represents the frequency (rad. s\textsuperscript{-1}) at which the maximum imaginary component occurs and α describes the degree to which the semicircle is depressed (α=1 represents a pure capacitor).

3.8.4 Supported Liquid membrane zinc permeation

In supported liquid membrane technology (SLM) extraction from a feed phase to a liquid membrane, diffusion through the SLM and re-extraction occur simultaneously. Di-2-ethylhexyl phosphoric acid (D\textsubscript{2}EHPA) is a cationic carrier (extractant) and was used in these studies to extract zinc ions from the cathode/feed chamber. The extractant was dissolved in kerosene and impregnated into a porous support.

The equilibrium reactions on the interfaces between feed/membrane and the membrane are given by the following equations:
3. Materials and Methods

\[ \text{Zn}^{2+} \text{[aq]} + 1.5 \text{(RH)}_2\text{[org]} \leftrightarrow \text{ZnR}_2\text{RH} \text{[org]} + 2 \text{H}^+ \text{[aq]} \]  

Equation 35

\[ 2 \text{ZnR}_2\text{RH} \text{[org]} \leftrightarrow 2 \text{ZnR}_2 \text{[org]} + (\text{RH})_2\text{[org]} \]  

Equation 36

And represents the condition at the liquid-liquid interface, where Equation 36 represents the condition in the organic-extract phase within the membrane. RH represents the extractant D$_2$EHPA and (aq) and (org) refer to aqueous (strip and feed phases) and organic phase, respectively (Pereira et al., 2007).

Figure 3-12: Schematic illustration of facilitated coupled counter transfer.

An important aspect of this process is the reversibility of the complex formed, so that Zn$^{2+}$ can be released into the strip phase at the interface II/III, according to facilitated coupled counter-transport for Zn|D$_2$EHPA|H$_2$SO$_4$ used in this study (see Figure 3-12).

### 3.8.5 BES construction and operation

The three chamber MFC/SLM integration reactors were machined from Perspex. The anode and strip chamber were cubic in shape (4 cm long and 3 cm in diameter) and the cathode/feed chamber (middle chamber) was 5 cm long and 3 cm in diameter. The chamber volumes were 25 ml for anode and strip chamber and 50 ml for the cathode. The anode was non-wet proofed carbon cloth (BASF, BIB, Somerset, USA). The cathodes were made from 30% wet proofed carbon cloth (BASF, BIB30WP, Somerset, USA). Additionally, four diffusion layers were applied with an airbrush on the air-facing side. A catalyst layer with 0.5 mg cm$^{-1}$ Pt and Nafion as a binder was then pasted onto the internal face,
according to the methods of Cheng et al. (2006). The two cathode electrodes were placed orthogonal to the anode and consisted of two air cathodes (3 x 2 cm) (see Figure 3-13). A silicon rubber gasket was used to seal the chambers and the cathode against to each other.

![Figure 3-13: Schematic illustration of the experimental set-up MFC/SLM reactor.](image)

The experiments in batch mode were carried out with 35wt% Di-(2-ethylhexyl)phosphoracid (D_{2}EHPA), the extractant or carrier for Zn^{2+} in the organic phase. In this case the extractant was dissolved in a hydrocarbon blend (ShellSol-T 100, Brenntag UK), which is insoluble in water. A porous polyethylene membrane (thickness = 0.63 mm, pore size distribution: 7-12 µm; Porex Technologies GmbH, Aachen, Germany) was impregnated with the organic mixture in an ultrasonic bath by submersion for 2h.

![Figure 3-14: Membrane module used in MFC/SLM experiments in batch mode.](image)

Three different experimental set-ups were tested and all experiments were carried out in triplicate. In the two chamber MFC configuration, the reactors were inoculated with 10%
anaerobic digestion sludge, 40 mM acetate in a nutrient 50 mM phosphate buffer media and operated under R = 1000 Ω external load, with tap water in the cathode chamber. Before the experiments were started, the bipolar membranes were replaced in all reactors and the impregnated SLM membrane was mounted between cathode/feed and strip chamber, in the MFC/SLM and SLM experiments. After the establishment of a stable voltage, the anode chamber was filled with 10 mM acetate substrate in the nutrient buffer media and the cathode chamber contained a synthetic wastewater with 400 mg L⁻¹ Zn²⁺ as sulphate. The strip chamber was filled with 40 g l⁻¹ sulphuric acid. The experiment was started by filling the cathode chamber (MFC) or the cathode and strip phase simultaneously (in the case of MFC/SLM, SLM) with the respective solutions; the MFC control was carried out with the same anode and cathode solution but sealed with a flat perspex sheet instead of the SLM. The experiments were stopped after 72 h. The MFC/SLM- and the MFC control reactors were each connected to a 1000 Ω external resistor and the voltages across the circuits were recorded every minute using LabVIEW™ software and an NI PCI-6224 I/O card (National Instrument Corporation Ltd., Bershire, UK).

3.8.6 Bipolar membrane

A bipolar membrane (fumasep®FBM, FuMa-Tech GmbH, St. Ingbert, Germany) of 0.18-0.20 mm thickness was employed with the cation exchange surface sited towards the cathode/feed chamber and the anionic exchange surface facing the anode, as reported by Heijne et al. (2006b, 2007b) and Wang et al. (2013b). Due to the MFC and SLM separation system integration, the same cathode/feed chamber was also separated from the strip phase by a supported liquid membrane, containing the organic phase, and the bipolar membrane used was placed with the anion exchange side towards the anode and the cation exchange side towards the cathode/feed chamber.

A water splitting reaction at the interface between CEM and AEM in the bipolar membrane transfers one proton and one hydroxyl ion to each respective chamber, so maintaining charge balance during electron transferred from the anode to the cathode. The dissociation of the water results in a theoretical membrane polarization of 0.830 V and is thought to be reversible even at high current densities (Hurwitz and Dibiani, 2001). Theoretically no buffer would be required in the anode as the protons produced by oxidation of the organic matter are neutralized by the hydroxyl ion transferred from the bipolar membrane (Wang et al., 2008b). However, in practice the anode and cathode
chamber solutions also contain ionic species, other than protons. These ions can be transferred into the transition area of the bipolar membrane, driven by a concentration gradient and *vice versa*, to maintain a current flow known as a leakage current (Kroll, 1997).

### 3.8.6.1 Membrane conductivity

The changes in the bipolar and liquid membrane conductivity during the time of operation were observed with electrochemical impedance spectroscopy in two electrode mode. The measurement was carried out with Ag–wire electrodes on either side of each membrane. The impedance spectrum was recorded over a frequency range of 300 000 – 0.01 Hz and was fitted to the following equivalent circuit:

![Equivalent Circuit Diagram]

The membrane conductivity was determined by using the equation below.

$$\sigma = \frac{L}{R \times A}$$  \hspace{1cm} \text{Equation 37}

Where $\sigma$ is the membrane conductivity in S cm$^{-1}$; $L$ is the membrane thickness (0.063 cm and 0.020 cm for liquid membrane and bipolar membrane, respectively); $A$ is the geometric membrane area (7.068 cm$^2$) and $R$ is the membrane resistance (Ω) fitted to the recorded impedance spectrum.

### 3.8.6.2 Permeability and diffusion coefficient

The membrane permeability $P$ (m s$^{-1}$) for Zn$^{2+}$ through the liquid membrane was calculated for the combination experiment $MFC/SLM$ as well as the $SLM$ control using were $c_{Zn}$ represents the zinc concentration in the cathode/feed chamber:

$$P = -\frac{V}{A} \times \frac{1}{\tau} \times \ln \frac{c_{Zn, \text{eq}}}{c_{Zn, \tau=0}}$$  \hspace{1cm} \text{Equation 38}

The diffusion coefficient $D$ (m s$^{-2}$) was determined by multiplying the membrane permeability by the membrane thickness.
3.8.7 Continuous Zn removal in MFC/SLM reactor

The continuous experiments were carried out in the same reactors than the experiments in batch mode. The middle chamber (cathode feed/chamber) was fed continuously with a 100 mg Zn²⁺ l⁻¹ solution at a flowrate of 70 ml d⁻¹ (ZnSO₄). The anode was operated in batch mode with 40 mM acetate in 50 mM PBS with vitamins and minerals.

Furthermore different strip acid concentrations were used in the strip chamber. Additional to the 40 g l⁻¹ H₂SO₄ tested in batch mode, 210 g l⁻¹ and 300 g l⁻¹ sulphuric acid were tested in the strip chamber. To distinguish between the different experiments the acid concentration is presented as part of the nomenclature in the graphs presented in chapter 8. A thicker membrane support was tested, when 300 g l⁻¹ H₂SO₄ was used; instead of the 0.6 mm, a 2 mm thick PE membrane was used with the same pore size distribution (7-12 µm; Porex Technologies GmbH, Aachen, Germany). The experiments in continuous mode were carried out with 35wt% and 40wt% D₂EHPA in kerosene (300 g l⁻¹ MFC/SLM experiment). Also a thicker PE membrane (thickness = 2 mm, pore size distribution: 7-12 µm; Porex Technologies GmbH, Aachen, Germany) was used to compare the performance. The membranes were impregnated in an ultrasonic bath for 2 h before placed in the reactors. Due to the different acid concentrations, the experiments were stopped whenever the substrate was depleted; hence there is a variation in the experimental duration. The 40 g l⁻¹ H₂SO₄ MFC/SLM was operated for 328 h and the 210 g l⁻¹ H₂SO₄ MFC/SLM for 280 h. The reactors were operated in batch mode for 16 h before they were switched into the continuous mode.

3.8.7.1 Zinc electrolysis

The zinc electrolysis was carried out in a reactor which had the same configuration and volume as the strip chamber (see Figure 3-15). The electrolysis (recovery of zinc) was carried out from four different electrolytes, where the sulphuric acid concentration (200 g l⁻¹ and 40 g l⁻¹) and the zinc concentration (10 and 70 g Zn²⁺ l⁻¹ as ZnSO₄) are adopted from industrial processes (see Table 2-2). A constant potential of 3.5 V was applied between the anode and cathode. The cathode was an aluminium sheet electrode, which was polished with fine sandpaper and a Pt wire was used as anode. The distance between the anode and cathode was kept to 2.5 cm. The measurement (10-20 min) was carried out under the action of a magnetic stirrer mixing the electrolyte.
The current yield was calculated by using the following formula:

\[
\text{Current yield} = \frac{\text{mass deposited}}{\text{theoretical mass deposited}} \\
\text{theoretical mass} = \frac{MM (Zn^{2+}) \cdot i \cdot t}{n \cdot F}
\]

Where \( MM \) represents the molar mass of zinc (65.39 g mol\(^{-1}\)), \( i \) the averaged current, \( t \) the time of electrolysis, \( n \) the number of electrons (Zn\(^{2+}, n=2\)), and \( F \) the Faraday constant (96 485.34 C mol\(^{-1}\)).

Figure 3-15: Electrolysis cell for the recycling of zinc.
4 Microbial fuel cells operating on real wastewater

This chapter deals with the use of a four-module tubular MFC as a polishing stage for a two stage Bio-H₂ and Bio-CH₄ production process. Furthermore, the wash down effluent from a food producing company high in VFAs (>1100 mg l⁻¹) was also considered as a feed in the same reactor, to determine the efficacy of the MFC system in reducing discharged of chemical oxygen demand (COD). The experiments presented in section 4.1.3 were carried out in a different tubular reactor which is introduced in section 3.8.1.3 and deals with different connection strategies (single module as well as 2, 3, 4 and five modules connected in parallel) and their effect on the internal resistance (capacitance and ohmic as well as charge transfer resistance changes) obtained from equivalent circuit modeling of EIS spectra.

Many studies on MFCs use acetate or other simple feed stocks such as glucose or saccharose to carry out studies in half cell conditions to specifically investigate the biofilm or performance of new materials for comparison reasons. Relatively few though increasing numbers of studies focus on the use of real wastewater in larger scale reactors. Hence there is a lack of knowledge in terms of how new materials and reactor designs in larger scale actually affect the performance when subject to real wastewater rather than synthetic waste streams. In general, the performance with respect to power production and wastewater treatment such as COD reduction will depend largely on the complexity of the feed waste stream provided as well as its conductivity. As it is important to test and compare the performance of different real wastewaters in the same reactor configuration, two different effluents were fed to a four module tubular MFC (see Figure 4-1). This should reveal limitations deriving from the type of wastewater in terms of power and parameters such as COD reduction or CE, such as they may exist.

Figure 4-1: Tubular four-module Microbial Fuel Cell with air-cathode.
4.1 Results

In this section the integration of a plausibly scalable MFC reactor (V=1 l) with anaerobic Bio-H₂ and Bio-CH₄ processes has been carried out, as was recently proposed (Premier et al., 2013b, F.R. Hawkes, 2010, Premier, 2010). Different organic loading rates were tested to investigate the effluent polishing ability at low organic loadings by connecting the MFC to a hydrogen fermenter and a methanogenic reactor. The performance was investigated in terms of power production, COD reduction efficiency, CE and energy conversion efficiency on the basis of the MFC’s influent COD as well as the effect on overall performance of the 3-stage (Bio-H₂, Bio-CH₄ and MFC) with changing influent COD concentration and associated OLR.

Furthermore washdown waters were fed to the same 4 module tubular reactor to investigate the potential for COD reduction of the effluent discharge. From this, an estimate of the expected reduction in the company’s discharge costs was made. Two different operating modes were tested, which differed in the amount of buffer and the operating strategy applied (constant load vs maximum power point tracking).

4.1.1 Series operation of a Tubular MFC on effluent from two stage Bio-H₂ and Bio-CH₄ process

![Diagram of MFC system](image)

Figure 4-2: 3-stage anaerobic process on wheatfeed for simultaneous biohydrogen, biomethane and bioelectricity generation.
4. MFCs operating on real wastewater

4.1.1.1 AD-effluent characteristics and operation

To avoid blockage of the reactor the effluent from the anaerobic digester was filtered through a stainless steel sieve to exclude solid particles ≥ 0.21 mm. The AD effluent characteristics were determined on a daily basis and contained on average 3.300 g COD l\(^{-1}\), of which 2.500 g COD l\(^{-1}\) were found to be soluble COD. The pH-value of the effluent was around 7.7 and exhibited a conductivity of 12.9 mS cm\(^{-1}\). The volatile fatty acids, namely acetic acid and butyric acid were found to be *circa* 80 mg l\(^{-1}\) and 30 mg l\(^{-1}\), respectively. Five different organic loading rates (OLR) (0.036; 0.053; 0.086; 0.337; 0.572 g sCOD l\(^{-1}\) d\(^{-1}\) designated OLR1 to OLR5, respectively) were tested and prepared by diluting the original Bio-H\(_2\)/Bio-CH\(_4\) reactor effluent. The final organic loading rate tested was beyond the rage of OLR1-5 in its sCOD concentration (6.149 g sCOD l\(^{-1}\)), which resulted in an OLR of 4.427 g sCOD l\(^{-1}\) d\(^{-1}\). This loading rate was also introduced to the MFC reactor and resulting performance compared to other loading rates (see Figure 4-6 and Figure 4-7). The AD-effluent was supplied at a constant flow rate of 0.5 ml min\(^{-1}\) through an external peristaltic pump (Watson and Marlow, Falmouth, UK), which resulted in a hydraulic retention time (HRT) of 33.3 h for the whole reactor or 8.3 h for each module. All four modules were independently connected to resistors (R = 1 kΩ) and operated at room temperature (20 ± 4°C), while the MFC influent was kept refrigerated at 4 °C.

4.1.1.2 Voltage development at different organic loading rates of two stage effluent

It can be seen, that the voltage increased with increasing organic loading (0.036-0.572 g sCOD l\(^{-1}\) d\(^{-1}\)) and decrease with the reactor lengths from module 1 to module 4 (effluent). This can be observed within one HRT of 33.3 h and is a result of the depleting organic substrate concentration reaching successive modules. The two lowest organic loading rates of 0.036 and 0.053 g sCOD l\(^{-1}\) d\(^{-1}\) exhibit a similar voltage output as can be seen in Figure 4-3. Furthermore, the fourth module produces virtually no voltage when the system is fed with the lowest OLR of 0.036 g sCOD l\(^{-1}\) d\(^{-1}\) and also shows a very low voltage generation from OLR2-OLR3. These results can be attributed to very low concentrations of degradable substrate, such as VFAs but may also be attributable to mass transfer limitations from the bulk to the biofilm/electrode interface, which are again driven by concentration gradient, at least in part.
4. MFCs operating on real wastewater

All the acetate and butyrate, which was present in very low concentration once dilution was used to adjust the organic loading, was likely to be consumed in the first modules. Even though the effluent from the OLR1 sampled after the fourth module still contained 32 mg COD l⁻¹, this organic content may not be available for direct conversion into electricity, but might be degradable in a longer MFC reactor with a greater number of modules. The effluent from the preceding two stage Bio-H₂/Bio-CH₄ process is usually burdened with recalcitrant or less biodegradable organic compounds such as hemicelluloses, holocellulose, α-cellulose, lignin, protein and starch. Even though the effluent was sieved to exclude larger particles which might block the reactor, the wastewater introduced to the MFC would still contain more complex compounds. These materials will become available through hydrolysis or other chemical or physical processes in their precession along the reactor lengths.

4.1.1.3 Power production in the tubular reactor

Figure 4-4 shows the power curves recorded for each module at each organic loading rate 0.036 – 0.572 g sCOD l⁻¹ d⁻¹ after 3 HRTs. It can be seen that maximum volumetric power density (MVPD) correlates with the organic loading and decreases with increasing module numbers, i.e. the distance along the reactor length. A significant increase in the maximum

---

Figure 4-3: Voltage generation from each module at different OLRs (0.036-0.572 g sCOD l⁻¹ d⁻¹) under R=1000 Ω.
power can be observed from OLR 1 to OLR 5; as the MVPD of each module increased from 0.010-0.018 W m\(^{-3}\) to 2.3-3.4 W m\(^{-3}\), respectively.

![Power curve for each of the four modules at different OLRs (0.036-0.572 g sCOD L\(^{-1}\) d\(^{-1}\)).](image)

The power was further increased when the undiluted effluent was fed to the reactor (5.5 W m\(^{-3}\)). It can be seen that smooth power curves were recorded in the first few OLRs, but the power overshoot phenomenon was observed from OLR 4 onwards. The higher power density with increasing organic loading is not only a result of the higher organic content, but also of the increasing conductivity which affects the internal resistance of the reactor. A similar tubular 2-module reactor (Figure 3-9) fed with synthetic sucrose wastewater, resulted in output power of 1.35 mW (5.4 W m\(^{-3}\)) in the first module with an organic loading of 0.41 g sCOD L\(^{-1}\) d\(^{-1}\) (Kim et al., 2010). Hence moderate power losses can be observed compared to the synthetic wastewater, as 0.82 mW (3.3 W m\(^{-3}\)) were produced in this experiment with OLR = 0.57 g sCOD L\(^{-1}\) d\(^{-1}\).
Table 4-1: MFC parameters during the continuous operation.

<table>
<thead>
<tr>
<th>OLR</th>
<th>pH</th>
<th>Conductivity</th>
<th>MVPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(gsCOD l⁻¹d⁻¹)</td>
<td>Inf.</td>
<td>Eff.</td>
<td>Inf.</td>
</tr>
<tr>
<td>OLR1</td>
<td>0.036</td>
<td>7.48</td>
<td>7.46</td>
</tr>
<tr>
<td>OLR2</td>
<td>0.053</td>
<td>7.55</td>
<td>7.46</td>
</tr>
<tr>
<td>OLR3</td>
<td>0.081</td>
<td>7.84</td>
<td>7.58</td>
</tr>
<tr>
<td>OLR4</td>
<td>0.337</td>
<td>8.45</td>
<td>7.65</td>
</tr>
<tr>
<td>OLR5</td>
<td>0.572</td>
<td>7.87</td>
<td>7.45</td>
</tr>
</tbody>
</table>

* Inf. and Eff. stands for the influent and effluent pH and conductivity
**The internal resistance in ohm (Ω) obtained at the maximum volumetric power density (MVPD) is present in brackets under the associated MVPD value.

Table 4-1 presents the pH, conductivity and the maximum volumetric power density (MVPD) as well as corresponding internal resistance. The influent pH was found to be between 7.48 and 8.45 and also the effluent pH values were found to be ≤ 7.65, showing that enough mixing was provided to avoid proton concentration gradients on the anode and cathode. Hence not only the higher organic content contributed to the increase in power but the higher conductivity also. It can be observed, that the power increased disproportionally from OLR4 to OLR5 (0.34 to 0.57 g sCOD l⁻¹d⁻¹), due to the increase in substrate availability and the increase in conductivity from 0.44 to 3.94 mS cm⁻¹. This is a consequence of the dilution, which significantly affected the ohmic losses and consequently the internal resistance of the reactor. Hence it should be kept in mind that if the Bio-H₂/Bio-CH₄ effluent is to be treated in a multi-modal reactor, in which the organic loading rate would naturally decrease due to the degradation of organic matter, the conductivity will not undergo such drastic reductions. Consequently higher power densities can be expected in a stacked multi-modal system, due to avoidance of such changes in the internal resistance.
4.1.1.4 COD and CE in a 4-module MFC on AD-effluent

The dependence of the influent organic loading on the CE and COD removal efficiency in the four modules of the tubular MFC is presented in Figure 4-5. A clear trend can be observed, where the sCOD removal efficiency is decreasing with increasing organic loading from 35.15% (OLR1) to 4.41% (OLR5), even though the specific COD removal increased in absolute terms, with 37 mg l\(^{-1}\) sCOD removed during the application of the highest OLR. This correlates with the average current produced in the four modules, which increased by more than 30 times from 0.069 mA (OLR1) up to 2.205 mA (ORL5).

When synthetic sucrose wastewater was used in a two module reactor, higher COD removal efficiencies were obtained (93-43% with 0.08-0.80 g COD l\(^{-1}\)d\(^{-1}\) (Kim et al., 2011a)). Hence if the reactor is fed with the Bio-H\(_2\)/Bio-CH\(_4\) effluent, a longer tubular system will be required to achieve effluent polishing, especially at high organic loading rates. A decrease in the COD removal efficiency with higher organic loading rates has been observed in other studies utilizing the effluents from an hydrogen biofermenter (Sharma and Li, 2010), a swine wastewater (Zhuang et al., 2012) and domestic wastewater (You, 2006).
In opposed to the COD removal efficiency, the CE increases with loading from OLR1 to OLR5 when using the Bio-H₂/Bio-CH₄ process effluent, as can be seen in Figure 4-5. When feeding the two highest organic loading rates (0.337 g sCOD l⁻¹ d⁻¹ and 0.572 g sCOD l⁻¹ d⁻¹), the CE increased up to 42% and 60%. The three lower organic loadings (OLR1-OLR3) resulted in CE between 3.9-9.5%. In general an opposite trend was observed, with high organic loadings resulting in a lower CE as presented in Figure 4-6, which also includes the highest organic loading tested of 4.427 g sCOD l⁻¹ d⁻¹ (undiluted Bio-H₂/Bio-CH₄ effluent). The same trend of increasing CE with the OLR was observed by (Kim et al., 2010), whereby the CEs obtained from the wheat-feed AD-effluent were higher than those from sucrose, which resulted in CE=38-49% at ORL=0.24 g sCOD l⁻¹ d⁻¹ in a two module tubular MFC. Several studies have shown the dependence of the CE on the substrate complexity and the substrate availability to electrogens. It was found that the CE with non-fermentable substrates such as acetate (CE=65%) are much higher as they can be consumed more directly by electrogenic bacteria. In contrast to easily degradable VFAs, fermentable
substrates such as starch or glucose resulted in significantly lower CEs of 21% and 14%, respectively (Min and Logan, 2004). The same was observed in another study, where the highest CEs were obtained using acetate (32%) and glucose (30%) and a lower CE was obtained for starch (19%) at substrate concentrations of 250 mg l\(^{-1}\) (Velasquez-Orta et al., 2011b).

Figure 4-6 summarizes previous studies conducted on MFCs operated in continuous mode fed on more complex substrates. To indicate trends, studies on sucrose wastewater (He et al., 2005, Kim et al., 2010), the effluent from fermentative hydrogen production (Sharma and Li, 2010, Nam et al., 2010b), domestic wastewater (Liu et al., 2004) or wastewater from a primary clarifier (Di Lorenzo et al., 2009c), in various reactor configurations and organic loading rates, were reviewed and presented together with the results from the Bio-H\(_2\)/Bio-CH\(_4\) effluent. Figure 4-6 also includes the CE determined when the undiluted Bio-H\(_2\)/Bio-CH\(_4\) effluent at OLR = 4.427 g sCOD l\(^{-1}\) d\(^{-1}\) was fed to the reactor, which resulted in a clearly lower CE of 3.6%. It can be seen that high CEs are only achievable at low organic loadings below 0.6 g COD l\(^{-1}\) d\(^{-1}\). The two studies carried out in the tubular reactor with two modules and sucrose (Kim et al., 2010) as well as the present study with four modules, resulted in an increase in the CE to a maximum at low organic loading. However, after peaking, the CE significantly decreases from 59.8% (0.572 g sCOD l\(^{-1}\) d\(^{-1}\)) to 3.6% with the undiluted effluent. This was also observed in other studies under continuous operation, using effluent from hydrogen fermentation on coffee processing wastewater, in which the CE decreased from 0.98% (1.92 g COD L\(^{-1}\) d\(^{-1}\)) to 0.3% (4.8 g COD L\(^{-1}\) d\(^{-1}\)) (Nam et al., 2010b) or from 5% (0.7 g COD L\(^{-1}\) d\(^{-1}\)) to 1.5% (6.5 g COD L\(^{-1}\) d\(^{-1}\)) (Sharma and Li, 2010). The peak observed in the studies using the tubular MFC might be attributed to mass transfer limitations at very low substrate concentration.

It can be concluded, that higher organic loading rates have a negative impact on the CE and that a multi-modular tubular reactor fed on complex waste streams may not deliver consistently high CEs. In a multi-modular reactor, the high organic loading rate introduced in the first few modules makes a significant amount of substrate available for methanogenesis, as the effluent itself contains methanogens and continually seeds the MFC with these microorganisms. Although power generation is not reduced in these modules, more substrate is available for methanogenesis and other side reactions related to the presence of alternative electron acceptor such as nitrate- or sulphate reducing bacteria or the presence oxygen in the anodic chamber (He et al., 2005, Logan et al.,
2006b, Schroder, 2007). Hence the competitive advantage of electrogens over methanogens will increase along the reactor length as the substrate concentration will also be lower and complex organic matter will be further degraded to lower carbohydrates and VFAs. This will increase the ratio of electrogens over methanogens, which is expected to positively affect the CE in consequence. Several methods to control the CE by diminishing methanogens; exposure to oxygen (Quan et al., 2012), low pH and temperature (Chae et al., 2010) or the addition of 2-bromoethanesulfonate (Zhuang, 2012), have been reported. Such methods are not necessary in a tubular reactor as it will only represent additional costs. The degradation of complex organic compounds along the reactor and the decreasing dominance of methanogens should result in an increasing CE with reactor length. Hence the CE will naturally vary in each module according to the affinity of electrogens towards the available substrate as opposed to methanogens.

The Figure 4-7 above shows the data fit for the determination of the pseudo-half saturation constant when including the highest organic loading rate of the undiluted yet sieved Bio-CH₄ effluent. The saturation concentration shows the region from which substrate concentration the power (or current) cannot be increased and presents a saturation characteristic. The saturation concentration for electrogens on the sieved AD-effluent is in the region of 6 g sCOD l⁻¹. As electrogens compete with methanogens or
other bacterial processes for the available substrate, the microbial affinity towards the available substrate is of great importance. The *pseudo*-half saturation concentration $K_s$ gives an indication of the affinity of electrogens towards the provided substrate. In order to determine the Monod-like $K_s$ value certain criteria, such as a limiting substrate concentration/availability has to be fulfilled (Rabaey et al., 2009). Furthermore factors such as the electrolyte conductivity, the reactor configuration and the load resistor used as well as other system specific parameters have to be the same. Therefore it has to be kept in mind, that the published $K_s$ values are all influenced by these variables which will have an impact when directly compared against each other. The *pseudo*-half saturation concentration for the 4-module tubular reactor fed on the BioH$_2$/BioCH$_4$ effluent resulted in $K_s = 436.6$ mg COD l$^{-1}$ ($R = 1000 \, \Omega$). The $K_s$ value for the two module tubular MFC on sucrose was $K_s = 50$ mg COD l$^{-1}$ under an external load of $R = 150 \, \Omega$ (Kim et al., 2010), and therefore more than 8 times lower than the $K_s$ value for the complex BioH$_2$/BioCH$_4$ effluent, indicating a lower affinity towards the more complex effluent. As mentioned above the higher load ($R=1000 \, \Omega$ in this study vs 150 $\Omega$) makes a direct comparison difficult and might have contributed to the higher *pseudo*-K$_s$ value, because similar OLR resulted in comparable power output and even higher CE. Furthermore mass transfer limitations at low organic loadings might have affected the determined *pseudo*-K$_s$ value and it is worth noting, that the $K_s$ value is based on COD, which only provides limited information on the composition and the ratio of easily degradable to complex carbohydrates, as VFAs are known to be the preferred substrate for electrogens.

4.1.1.5 Energy efficiency of a four module tubular MFC and its dependence on the organic loading rate

Massanet-Nicolau et al. (2013) have shown that the anaerobic two-stage process on wheat-feed increased the methane yield by 37% compared to the single stage fermentation. To further reduce effluent COD and increase the energy recovery from wheat-feed pellets fed to the system, a tubular four-module MFC reactor was fed with the two-stage effluent at different OLRs. Table 4-2 presents the energy recovered by COD consumed ($E_{\text{COD}}$). It can be seen, that the $E_{\text{COD}}$ correlates with the organic loading rate and reaches its highest value of 0.276 Wh gsCOD$^{-1}$ at the highest organic loading rate (0.572 g sCOD l$^{-1}$ d$^{-1}$); OLR 1 resulted only in 0.001 Wh gsCOD$^{-1}$.
4. MFCs operating on real wastewater

<table>
<thead>
<tr>
<th>OLR</th>
<th>( E_{\text{COD}} )</th>
<th>( E_R )</th>
<th>( E_{\text{Infl.}} )</th>
<th>( \text{ECE}_{\text{total COD}} )</th>
<th>( \text{ECE}_{\Delta \text{COD}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g sCOD l(^{-1}) d(^{-1}))</td>
<td>(Wh g( \text{sCOD} l^{-1} ) consumed)</td>
<td>(J l(^{-1}))</td>
<td>(J l(^{-1}))</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>OLR1</td>
<td>0.036</td>
<td>0.001</td>
<td>0.33</td>
<td>686 – 1147</td>
<td>0.03 – 0.05</td>
</tr>
<tr>
<td>OLR2</td>
<td>0.053</td>
<td>0.003</td>
<td>0.41</td>
<td>1028 – 1721</td>
<td>0.02 – 0.04</td>
</tr>
<tr>
<td>OLR3</td>
<td>0.081</td>
<td>0.004</td>
<td>2.96</td>
<td>1570 – 2627</td>
<td>0.11 – 0.19</td>
</tr>
<tr>
<td>OLR4</td>
<td>0.337</td>
<td>0.166</td>
<td>42.62</td>
<td>6994 – 11703</td>
<td>0.36 – 0.61</td>
</tr>
<tr>
<td>OLR5</td>
<td>0.572</td>
<td>0.276</td>
<td>92.95</td>
<td>11543 – 19313</td>
<td>0.48 – 0.81</td>
</tr>
</tbody>
</table>

The energy recovered through the four modules of the reactor increased from 0.33 J l\(^{-1}\) (OLR1) to 92.95 J l\(^{-1}\) (OLR5). These values are based on the assumption that each of the four modules operates at the maximum power point (as presented in Figure 4-4) for an entire HRT of 8.3 h. A higher energy recovery of 259 to 337 J l\(^{-1}\) with higher OLRs of 0.61 to 2.35 g COD l\(^{-1}\) d\(^{-1}\) was achieved by Sharma and Li (2010) with a synthetic glucose feed. Also the two-stage process operated at a significantly smaller scale with 2 l bio-fermenter and 0.1 l MFC. However, in their study a further increase in the organic loading also resulted in a lower energy recovery.

The energy conversion efficiencies (\( \text{ECE}_{\text{total COD}} \), \( \text{ECE}_{\Delta \text{COD}} \)) of the tubular MFC with four modules are presented in Table 4-2. \( \text{ECE}_{\text{total COD}} \) are calculated based on the total energy content of the MFCs influent and \( \text{ECE}_{\Delta \text{COD}} \) is calculated with respect to the COD removed. \( \text{ECE}_{\text{total COD}} \) was between 0.03-0.05% at OLR1 and 0.48 – 0.81% at OLR5 and \( \text{ECE}_{\Delta \text{COD}} \) resulted in higher values of 0.08- 0.14% (OLR1) and 10.9 - 18.24% (OLR5).

The energy recovery (\( E_R \)) increases with the organic loading rate, which is attributed to the substrate availability and correlates with the CE. The energy conversion efficiency in terms of the consumed COD (\( \text{ECE}_{\Delta \text{COD}} \)) is lowered by the amount of energy necessary to maintain the bacterial metabolism. Hence the total theoretical Gibbs Free Energy (G) content of the substrate cannot be converted with 100% efficiency. Schroeder (2007) reported, that only
54% of the total Gibbs Free Energy of glucose can be transformed into electricity. Furthermore McCarty et al. (2011) reported that some of the energy will be dissipated (approximately 15%) to losses associated with microbial growth, maintenance and carbohydrate conversion into methane; hence similar losses can be expected for electrogens, and the conversion of VFAs into electricity, electrogenic electron transfer reactions and carbohydrate conversion. Further losses derive from the cell potential efficiency, as the theoretical maximum thermodynamic cell potential of an MFC is lowered by activation losses, ohmic losses and mass transfer losses.

The calculation of the energy conversion efficiencies is based on the heat of combustion values, which includes the non-biodegradable fraction of the wheatfeed and will not be available for substrate to electricity conversion at any point. Furthermore it should be kept in mind that the values on which the calculations are based vary depending on the wastewater used, so more accurate values will be available if the energy content of the Bio-H$_2$/Bio-CH$_4$ effluent were to be determined in a calorimeter. The energy conversion efficiency for the total COD (ECE$_{total\ COD}$) depends on the bio-degradability and the recalcitrant in the AD effluent/MFC influent of the substrate. Due to the complexity, the values reported in Table 4-2 are significantly lower than for less complex synthetic wastewater, as the influent of the MFC has already passed two biological process stages (hydrogen fermenter and anaerobic digester). ECEs in earlier studies presented higher values; 42% for acetate compared to 3% for glucose in batch mode (Lee et al., 2008a). A study by Min and Logan (2004) in continuous mode resulted in an ECE of 17% for acetate and 3% for glucose. The addition of further modules can increase the ECE, as more modules can further degrade the complex compounds in the waste and make them available for electrogens. Also the ohmic losses would be lower (no dilution with tap water), which will also positively affect the ECE.

4.1.1.6 Estimation of energy efficiency for the three stage bio-hydrogen, bio-methane and bioelectricity producing process

The biogas and electricity production were normalized specifically to the COD content of the original wheat-feed. The bio-hydrogen and bio-methane produced have specific energy contents of 55.15 kJ kgCOD$^{-1}$ and 9,852.5 kJ kgCOD$^{-1}$ respectively (Massanet-Nicolau et al., 2013). The contribution of the MFC is 4.76 kJ kgCOD$^{-1}$ of the original feedstock, when the remaining COD in the BioH$_2$/BioCH$_4$ effluent was provided at an OLR.
of 0.574 gsCOD l⁻¹ d⁻¹.

In total, between 42.63-71.36% (ECE₃stage) of the total energy content of wheat-feed (13.896-23.250 kJ kgCOD⁻¹, depending on referenced assumptions) could be recovered in one of the three energy carriers. However, almost all the conversion efficiency (ECE₃stage), derives from the bio-methane production (42.38-70.93%), whereas the bio-hydrogen and bioelectricity production only contributes 0.24-0.40% and 0.02-0.03% to the total energy recovery in this study. It is important to note again, that the results refer to a limited four module MFC reactor operating on digestate and therefore a multi-modular MFC has the potential to recover more energy. Also, the effect of the bio-hydrogen stage on the bio-methane performance has not been considered here.

In general the biodegradable portion of the feed will affect the ECE as all three stages can only utilize this fraction. The heat of combustion however, also includes the recalcitrant or non-biodegradable fractions. Furthermore, we might consider that 60-70% of the energy of bio-methane is lost in heat when converted into electricity using a heat engine (McCarty et al., 2011). Hydrogen PEM fuel cells have an energy efficiency which lies between 30-60% at T=50-100 °C (Sorensen, 2005), with a theoretical maximum efficiency of 83%, based on the higher heating value (Feroldi and Basualdo, 2012) and may require gas clean-up. The MFCs energy recovery must be improved if it is to justify their use beyond effluent polishing in the system presented. However, MFCs convert the organic content directly into electricity, and show potential for cost savings by reducing COD discharge to sewer, which may represent sufficient advantage with further improvement of efficiency and system configuration.

### 4.1.2 Food production washdown waters as fuel for tubular Microbial Fuel Cells

In the following section the results obtained on the food-producing industry wastewater in the same four-module tubular MFC are presented. The study aims to reduce the COD concentration and enhance the bioelectricity generation. The washdown water from the food producing company was operated in two different modes in the same four module reactor, which differed in terms of buffer concentration (PBS; 35 mM vs 3 times 50 mM), circuit control (100 Ω static load vs MPPT control) and operation (steady state vs continuous cycle). Information on the washdown water composition and details on the operation mode can be found in section 3.8.1.1.
4. MFCs operating on real wastewater

### 4.1.2.1 Soluble COD reduction in tubular 4-module reactor on washdown water

The COD reduction in both operating modes is presented in Figure 4-8. It can be seen that after 7 cycles 84% or 960 mg l\(^{-1}\) (from 1140 mg l\(^{-1}\) to around 200 mg l\(^{-1}\)) were removed in mode A and 70% (800 mg l\(^{-1}\)) in mode B with respect to the effluent concentration. Therefore mode A resulted in a higher reduction efficiency, but it should be kept in mind that during the 3 days of each cycle, natural (probably aerobic) degradation might have also occurred in the bottle itself, which is not related to power production. From Figure

![Figure 4-8](image_url)

**Figure 4-8:** Soluble COD reduction (a) and the reduction in sCOD in each of the 7 cycles at two different sampling points (module 4 and the effluent) (b) in operation modes A and B.
4-8 it can be seen that mode A and B give different degradation curve shapes, so that the sCOD was reduced by 55% after 3 cycles (12 modules) in mode A, whereas mode B resulted in only 21% reduction after the same cycle number. This difference might be attributed to the fact that the 7th cycle ended after 18 days (mode A) but after only 7 days in mode B. The control solution stored in the fridge (CF) and at ambient temperature (CRT) resulted in sCOD removal of 300 mg l⁻¹ and 290 mg l⁻¹ after cycle 7 (MPPT mode; 7 days) and were therefore significantly lower than the results achieved by bioelectrochemical treatment in the microbial fuel cell. These results indicate that MFCs might be able to reduce COD discharge costs significantly.

4.1.2.2 Reduction of volatile fatty acids

Figure 4-9 presents the changes in VFAs for both modes, whereby only acetic and propionic acid are considered, as the concentration of higher molecular weight acids is negligibly small. The acetic acid degradation behavior correlates with the COD reduction in Figure 4-8. Therefore it could be deduced that the sCOD degraded in mode A was mostly attributed to the concentration of volatile fatty acids. Conversely, mode B resulted in an increase in acetate concentration in the cycles 1 to 3, before it sharply decreases to zero after cycle 6.

Also the concentration of propionic acid increased during cycles 1-5. This increase is believed to be due to the breakdown of higher carbohydrates to VFAs. Therefore the acetic and propionic acid concentrations are not only decreasing because of their use as substrate for electrogenic bacteria, but are also increasing due to degradation processes, although carbohydrate concentrations were not measured explicitly. In the proposed case that there was additional VFA production, these VFAs would be seen to be consumed as the concentration of VFAs went down to zero in the latter cycles. Similar was observed by Velasquez-Orta et al. (2011a), where MFCs fed with brewery wastewater exhibited a transient increase in VFA before it was consumed.

The VFA depletion behaviour indicates that the bacteria in the mixed culture biofilm show a higher affinity towards acetic acid than towards propionic acid. The two control solutions (see table 12.3) resulted in a clearly higher end-concentration of acetic acid (220 mg l⁻¹ CRT and CF) and propionic acid (155 mg l⁻¹ CRT and 133 mg l⁻¹ CF), as can be seen in Figure 4-9.
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4.1.2.3 pH and conductivity changes in mode A and B

The changes of the pH and the conductivity are illustrated in Figure 4-9 for both modes A and B. In general, the oxidation of organic substrate by electrogenic bacteria releases protons, which are used for the ORR. Hence under ideal condition the pH stays the same throughout the operation, which was also observed when the unbuffered effluent from the two stage Bio-H₂/Bio-CH₄ process was used. In real operation, pH increase in the anode chamber is a common phenomenon, as the cation exchange membrane is permeable to other cations, probably present in higher concentration, which can also

Figure 4-9: Acetic acid (a) and propionic acid (b) degradation in a four module tubular MFC on washdown water effluent in mode A and B.
MFCs operating on real wastewater maintain the required charge balance. The arrows indicate the addition of PBS buffer, which only refers to mode B. In mode A 35 mM buffer were added to the washdown water, hence the influent was buffered once at the beginning. In order to avoid pH below 6 the pH was also adjusted twice during operation with PBS buffer (50 mM) in mode B.

Figure 4-10: pH (a) and conductivity changes (b) during 7 cycles of operation. The arrows point out the addition of 50mM PBS buffer, which refer to mode B.
These points in time can be clearly identified from Figure 4-10 b as sharp increases in the conductivity after cycle 3 and 6. Even though a higher buffer concentration was used in mode B than in mode A, the pH decreased more rapidly under these operation conditions (MPPT mode). Based on these results the COD reduction must be higher in mode B, as the proton concentration (pH value) is directly related to the COD reduction; however this higher COD reduction in mode B was not observed (see Figure 4-8).

The pH of the control solutions does not undergo significant changes due to the buffering. Also the conductivity changed little, dropping from 7.45 mS cm\(^{-1}\) to 6.82 mS cm\(^{-1}\) in the CF, whereas the CRT exhibited the same conductivity even after 7 cycles compared to that observed at the starting point.

### 4.1.2.4 Voltage development of four module MFC on washdown waters

Before the first cycle was started, the system was operated for 3 HRTs under 1000 \(\Omega\) to acclimatize the bacterial community to the waste (see Figure 4-11 (a) - 0 cycle). During this period of time a power curve was measured (see Figure 4-12 (a)). The potentiostatic power curve measurement resulted in an open circuit potential of 600 mV and a maximum volumetric power point of 5.86 W m\(^{-3}\) at \(R = 85 \Omega\).

Another power curve was recorded for module 1 during the 2\(^{nd}\) cycle, which leads to a lower maximum volumetric power point of 3.34 W m\(^{-3}\), due to the lower organic loading rate, the lower pH-value as well as the lower conductivity and substrate availability. However, maturation of the biofilm is evident from the spreading of the power curve, in Figure 4-12. No power curve was recorded in mode B, as the short cycle time of 24 h might influence the measured COD reduction.
Figure 4-11: Voltage development of each of the four modules in mode A (a) and mode B (b).

Figure 4-12 (b) shows the power produced in all four modules in mode B, using the MPPT control system. The power development in mode B shows that the buffer addition, especially after cycle 3, resulted in a clear increase in power due to the lower internal resistance. The addition of buffer after cycle 6 did not have a positive impact and confirms the depletion of easily degradable substrate (VFAs) as observed in Figure 4-9. The total Coulombic Efficiency based on the COD reduction for all 7 cycles was calculated to be
66.58% based on the reduction of 985 mg l\(^{-1}\) sCOD in mode B with MPPT control. The charge produced in four modules in the cycles 1 to 6 were found to be between 1085 Cs and 1322 Cs and only the charge produced in the last cycle was significantly lower (480 Cs).

Figure 4-12: Power curves measured during cycle 0 and 2 in mode A (a), power and energy production in mode B with MPPT control (b).
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4.1.2.5 Discharge cost savings

The costs savings are calculated based on the Mogden formula see equation 31 (page 64) whereby only the discharge costs for COD has been considered \((B \cdot O_t/O_s)\) with \(B = 0.2353\) and \(O_s = 500\) mg l\(^{-1}\) (WelshWater, 2013)). It should be kept in mind, that the tariffs and calculations are based on the soluble COD concentration, which will increase during the treatment, due to the degradation of higher carbohydrates. The cost savings for discharging the washdown effluent can be significant if all the COD becomes available with increasing cycle number (which can be roughly correlated to the number of modules required). Within only four modules the cost savings are 0.132 £ m\(^{-3}\), and increases to 0.463 £ m\(^{-3}\) after seven cycles (28 modules).

![Figure 4-13: Discharge cost savings after 7 cycles based on the reduction of sCOD.](image)

4.1.3 Internal resistance of tubular MFC with parallel connected modules

In this section a different five-module reactor was used (see section 3.8.1.3) to determine changes in the reactor impedance, as explained in more detail in a contemporaneous thesis (Boghani, 2014). A modularized and scaled-up reactor, which contains five hydraulically connected modules was studied, with an increasing number of modules connected electrically in parallel; whereby the different modes refer to module 1 only (mode A), module 1+2 in parallel (mode B), module 1+2+3 in parallel (mode C) and module 1+2+3+4 in parallel (mode D). In this section only the results from EIS measurements
4. MFCs operating on real wastewater

taken from the different modes are presented, whereas the remaining data collected from this reactor can be found in the thesis by Boghani (2014).

4.1.3.1 Internal resistance of tubular MFC

In general the internal resistance of Microbial Fuel cells can be determined with different methods (polarisation plot, resistance at the maximum power point, current interrupt), including EIS used in this study. From Figure 4-14 it can be seen, that the internal resistance is very low (<7.5 Ω) and the decreases with the number of modules connected in parallel, which was also observed for the ohmic and polarisation resistances. The total internal resistance was measured to be 6.25 Ω, 3.78 Ω, 2.31 Ω and 1.45 Ω for mode A, B, C and D, respectively. However, the hydraulic connection between the modules might cause losses due to the liquid phase interconnection between the modules. Zhuang and Zhou (2009) found that there is a voltage loss of 36% when the cells are hydraulically and electrically connected. The same potential drop of unit cells connected in series was also observed by Kim et al. (2012a) due to ions on the anode electrode traveling through the electrolyte to be reduced at the cathode. In general it was found that these losses can be minimized by increasing the distance between the unit cells. The results regarding the

![Figure 4-14: Internal resistance in the different operation modes and the proportion of ohmic, anodic- and cathodic polarization resistance.](image-url)
losses from the parallel connection due to the hydrodynamic connection of the modules was carried out by Boghani and is presented in his thesis (Boghani, 2014).

The ohmic resistance determined by EIS, caused mainly by the solution and membrane resistance, decreased from 3.04 Ω down to 0.80 Ω, which represents a reduction of 80.7% compared to the ohmic resistance in the first module (mode A). The electrolyte resistance depends on the conductivity (ionic concentration, type of ions and their valence value) as well as the temperature. Furthermore the internal resistance will also contain the membrane resistance, resistance of electrodes/connection as well as the resistance of the biofilm itself.

The charge transfer resistance of the cathode and anode ($R_c$ and $R_a$) followed the same trend and decreased with increasing number of modules connected in parallel (see Figure 4-14). $R_a$ decreased by 48%, 66% and 74%, and $R_c$ decreased by 10%, 48%, 72% in mode B, C, D (compared to mode A); whereby the polarisation resistance of the anode is approximately one order of magnitude smaller than the polarisation resistance of the cathode. This result is typical for microbial fuel cells, as the bacteria themselves act as biocatalyst. Biological catalysts are known to have low charge transfer resistance as the bacterial metabolism will influence the electron transfer rates. A decrease in the charge transfer resistance due to biofilm formation has been observed in the past and indicates their catalytic properties (Ramasamy et al., 2008, Borole et al., 2009).

One key factor for a low anodic charge transfer resistance is the tendency of the bacteria to grow and “stick” to the electrode, which will largely affect the biofilm formation. This implies a strong dependence of the charge transfer resistance on the electrode material. In general the material of choice should exhibit a good biocompatibility, chemical stability, good electrical conductivity and a large surface area. Different carbon materials such as graphite rods, graphite fiber brushes, carbon cloths, carbon papers, carbon felts, and reticulated vitreous carbon (RVC) are common in microbial fuel cells. In this study carbon cloth was used as the anode material as it is known to give a thick biofilm and also because of its relatively low cost and resistance. Other materials investigated such as gold (Crittenden et al., 2006, Sun et al., 2010) and certain types of stainless steel (Dumas et al., 2007) were found to have lower affinity for bacterial growth and resulted in lower power densities. Also titanium was used as an anode material but was found to be unsuitable as an anode material (ter Heijne et al., 2008). Furthermore surface modification of anodes with conductive polymers, such as polypyrrole or polyanilin with positive functional
groups (Yuan and Kim, 2008, Feng et al., 2010, Kaur et al., 2014) were found to enhance the biofilm attachment due to electrostatic interactions of the functional groups introduced, with charged groups on the outer bacteria cell membrane. It was also reported that the polarisation resistance depends on the age of the biofilm, which implies that the biofilm development improved the kinetics of the electrochemical reaction (Ramasamy et al., 2008). Hence the polarisation resistance here reported might decrease with time, as the measurement was carried out at an early stage of the biofilm formation (approximately 1 month after inoculation).

The cathodic charge transfer resistance is significantly higher than the anodic charge transfer resistance, as illustrated in Figure 4-14. These results indicate that the oxygen reduction reaction is slower than the acetate oxidation on the anode. The higher cathodic charge transfer resistance is also affected by the membrane attached to the cathode as well as the pH of the solution (Jung et al., 2011), as He and Mansfeld (2009) reported a decrease of the cathodic polarisation resistance with increasing pH.

### 4.1.3.2 Capacitance of tubular MFC in different connection modes

Figure 4-15: Capacitance of the anode and cathode measured via impedance spectroscopy.
In the reactor under investigation, the double layer capacitance is caused by charge separation between the electrode and the electrolyte, the electrode/biofilm/electrolyte interface as well as the electrolyte/membrane/electrode interface. The double layer capacitance depends on various components such as electrode polarization, ionic concentration, temperature, type of ions, oxide layers and roughness of the electrode.

The increase in capacitance in the different operation modes results from the parallel electrical connection as the total capacitance represents the sum of capacitance in all modules. The total capacitance increased from 0.53 F (mode A) to 2.24 F (mode B) and the cathode capacitance was found to be significantly higher than the anodic. The anodic capacitance increased by 2.7 times from 13 mF (mode A) to 35 mF (mode D); whereas the cathodic capacitance increased by 4.3 times from 520 mF to 2210 mF. Therefore the capacitance results show no diminution due to the serial hydraulic connection.

The higher capacitance observed for the cathode can be attributed to the large surface area of carbon cloth for the build up of a double layer at the electrode/electrolyte interface as it exhibits a relatively high specific surface area of 1038 m² g⁻¹ measured by BET analysis as reported by Zhao et al. (2009). This is due to the surface modification of the cathode (a catalyst layer containing carbon and Pt powder with Nafion as a binder, applied on the solution-facing side of the cathode), which enhances the specific surface area of carbon cloth. Furthermore the cation exchange membrane, which is directly attached to the cathode, also builds up a double layer on the interface. Hence the electrode material and modifications, affect not only the polarisation resistance but also the double layer capacitance.

4.2 Discussion

Two different wastewater types (effluent from a two stage anaerobic process, washdown water from a food producing company), both relatively high in VFAs were used in a four module tubular MFC reactor to test performance related parameters such as power density, CE and COD removal efficiency as well as energy conversion efficiency (ECE). Apart from the VFA concentration, another advantage that both wastewater exhibits is the higher conductivity compared to domestic wastewater.

When the effluent from a two stage Bio-H₂/Bio-CH₄ process was used as a fuel source, the voltage and power production were found to correlate with the organic loading rate
4. MFCs operating on real wastewater

(0.036 to 0.574 g sCOD l\(^{-1}\) d\(^{-1}\)), hence it increased with the OLR and decreased within the four module according to their position along the reactor length. The COD removal efficiency lies between 35% at the lowest OLR and 4.4% at 0.572 g sCOD l\(^{-1}\)d\(^{-1}\). The comparison with other studies showed that the CE decreases significantly at higher organic loading rates, with more complex waste streams.

In the case of the washdown water from the food producing company, higher organic loadings were chosen starting at 2.79 g sCOD l\(^{-1}\) d\(^{-1}\), but a lower resistance of R=100 Ω was used (mode A) or MPPT control (mode B) to increase the COD removal rate. The organic loading rate decreased to 0.53 g sCOD l\(^{-1}\) d\(^{-1}\) and 1.00 g sCOD l\(^{-1}\) d\(^{-1}\), in mode A and B respectively; which is comparable to the highest organic loading rate when Bio-H\(_2\)/Bio-CH\(_4\) effluent was used. In general a better performance in terms of power production and COD reduction was observed. Apart from the OLR, the conductivity was also found to have a big impact on the performance. While the conductivity in the 3 stage system was around 0.44-3.98 mS cm\(^{-1}\), the conductivity with the food producing effluent was higher in both modes (3.7-3.0 mS cm\(^{-1}\) mode A and 7.45-12.1 mS cm\(^{-1}\) in mode B), which is a result of the buffer addition. In the MPPT controlled mode B it was even necessary to adjust the pH during operation, by adding 50 mM buffer. This shows that even though a higher flow rate was chosen for the washdown water (0.5 ml min\(^{-1}\) vs 0.69 ml min\(^{-1}\)) the mixing was not high enough to avoid pH gradients. This also indicates that the washdown water was less complex than the AD-effluent and provided more substrate for electrogens (VFAs) – see Figure 4-9. This is in accordance with the higher COD reduction in absolute terms observed with the washdown water. The faster degradation of organic matter produced more protons and the higher proton release was only partially compensated by the buffer added and could not avoid pH gradients at a later stage. Also the importance of VFAs for the power production was clearly proven, as the power generation in mode A diminished below 1 W m\(^{3}\) after 6 cycles, due to the lack of VFAs. Furthermore it was observed that this buffer addition increased the power in mode B, but did not affect the COD degradation. Hence the increase in power was more likely a result of the lower internal resistance and did not enhance the COD degradation.

The results indicate that a significant amount of the soluble COD can be removed by anaerobic treatment in a microbial fuel cell. If operated in mode B with continuous circulation and maximum power point system control, the sCOD removal increased from 280 mg l\(^{-1}\) (24%) after cycle 1 to 984 mg l\(^{-1}\) (84.8%) after cycle 7; after 6 cycles 774 mg l\(^{-1}\) (65.5%) of sCOD had been removed in mode B. In general it was shown that the COD
reduction can be enhanced if the systems internal resistance is matched with the external resistance for the whole period of operation (maximum power point tracking control).

During the operation with the washdown water, two anaerobic controls were set aside at room temperature and at 4 °C to observe mainly changes in COD and VFAs, without the contribution of electrogens. There was only a small difference between different temperatures and after 7 cycles the effluent contained 215 mg l⁻¹ acetic acid and 141 mg l⁻¹ propionic acid. By contrast, all of the acetic acid was consumed in the MFC, showing that a MFC can significantly enhance the degradation. However, it has to be kept in mind, that COD can also be degraded under anaerobic condition in the absence of electrogens (MFC). The values of the controls in terms of acetic- and propionic acid, COD, conductivity and pH during the 7 cycles can be found in table 12.3.

The energy conversion efficiency (ECE) over four modules, calculated based on the COD consumption showed that the highest efficiency ($E_{\Delta\text{COD}}$) was in the range of 10.9 - 18.24% (OLR5). The energy recovery based on the total influent energy content lies between $E_R = 11.5-19.3$ kJ l⁻¹ and resulted in a significantly lower energy recovery of 0.48-0.81%. Furthermore the energy conversion efficiency over the entire three stage process was calculated and was found to be 71.36%, based on an energy content of 13.896 kJ kgCOD⁻¹ (Owen, 1982). 70.93% accounts for bio-methane production and only 0.40% derived for bio-hydrogen and 0.02% from bioelectricity production.

The theoretical maximum energy that can be extracted from an MFC with air-cathode system is minimized by several factors. It will depend on the total Gibbs free energy (G) of the organic mixture provided in the waste, which will be lowered by the CE and will further be diminished by the energy necessary to maintain the microbial metabolism. Further losses are caused by the reactor configuration and materials and derive from the activation polarization on the anode and cathode, ohmic losses (which will be influenced by the reactor configuration and conductivity of the wastewater) and concentration polarization. The power requirements for operating the system will derive primarily from the need to deliver the effluent to and through the process. A further demand may derive from control mechanisms that might be applied to manage the current sourced from the microbial fuel cells.

MFC treatment of wastewaters is still at an early stage of development and the system used was not of a sufficient scale to represent a multi-module (28 MFCs) which the
experimentation tried to marginally emulate by recirculation. This approach is believed to have affected the performance of the biocatalyst a negative sense; due to the time (two out of three days) the effluent was left untreated in mode A. The MPPT system installed (mode B) helped to extract the maximum power, but was found to be limited by the amount of acetic acid present in the waste stream. Also a better performance can be expected from the fact that the development of the biocatalyst would be spatially selected depending on the position along the tube and hence the state of oxidation of the effluent COD. In general the HRT has to be adjusted to the waste complexity, taking appropriate mixing into account.

There are challenges which remain and need to be overcome before the technology could be deployed commercially, some of which are evident in the work reported here. In general higher power densities have to be achieved in scaled up reactors to make them suitable for real application. This may be difficult to achieve as the electrode surface area is not proportional to the power output (Dewan et al., 2008, Cheng and Logan, 2011). Also, the addition of phosphate buffer to modulate the pH and affect conductivity (hence performance) is not expected to be a viable and economic approach. A subsequent tubular reactor design used in the EIS study on electrically parallel connect modules, consists of a helical anode, which provides better mixing, lowers mass transfer losses and might be able to avoid pH-gradients between the anodic biofilm and the cathode. Hence certain limitations can be ameliorated by the reactor design and the choice of material, but others such as complexity and conductivity will be governed by the type of waste provided as a fuel.

4.3 Conclusion

A tubular  4- module reactor was tested for its suitability in real application and was found to be an appropriate design for wastewater treatment and effluent polishing. In general the experiments have shown that the performance will largely depend on the complexity of the organic matter provided and above all on the VFAs, mainly acetic acid content. However, the conductivity also plays a major role on the internal resistance of the cell and limits the power production. To decrease the internal resistance and enhance the current to a useful level, different number of modules can be connected in parallel.
The effluent from a two stage anaerobic process fed on wheatfeed and washdown water from a food producing company were tested as fuels. Depending on the complexity of the wastewater, more modules would be required to degrade higher carbohydrates into VFAs, which will be consumed preferentially by electrogens along the reactor’s length. Hence in a multi-modular reactor the organic loading rate and consequently the CE will vary along the reactor.

The reactor impedance depends largely on the electrolyte and therefore on the conductivity of the waste streams. The addition of buffer was found to increase the performance of MFCs fed on real wastewater, but is not considered sustainable as buffering will incur costs and might require further treatment steps.
5 Duty cycling to enhance power quality in tubular MFC

There are several ways to increase the power density of MFCs, some of which are discussed in this thesis. Power density may be increased by optimizing the reactor configuration, by applying maximum power point tracking methods or by improving the cathode side and reduce overpotential losses, for example. The typical voltage level output from a single MFC is normally not high enough to power commercially available low power consuming electronic devices. Apart from increasing the MFC voltage, other methods have been suggested, such as external capacitor, DC/DC converters (Degrenne et al., 2011) and also there is the possibility to connect unit cells in series or parallel (Zhuang and Zhou, 2009, Logan et al., 2006c, Jafary et al., 2013) to increase the current and/or voltage.

In this chapter the intrinsic capacitance effect of an entire tubular MFC reactor as described in section 3.9.3, but especially the anode with its high surface area, was investigated to determine if alternating open and closed circuit operation could enhance the power quality by using the phenomenon of charge accumulation in the MFC which presents, due to various mechanisms, a pseudo-capacitance. Several studies have investigated capacitance in microbial fuel cells, but these have generally been in half cell conditions (Schrott et al., 2011, Uría et al., 2011, Deeke et al., 2012). In this study the total capacitance of a tubular MFC was considered as tool to enhance the power output quality (primarily voltage) and hence the applicability of the MFCs.

5.1 Results

The results presented in this chapter deal with the capacitance of a tubular 2-module reactor with high surface carbon veil anode, as presented in section 3.9.3. The pseudo-capacitance was investigated by observing the dynamic cell-, anode- and cathode response. The capacitance of the whole cell as well as the capacitance of just the anode compartment, made evident during on/off operations with different open and closed circuit times, were investigated under different external loads in order to quantify any additional energy and/or power which may be accumulated during open circuit (OC)
operation and then made available after reconnection to an external load in closed circuit (CC) operation. Also, an automated on/off switching mechanism was implemented to periodically connect a 100 Ω external load and the anodic impedance spectra were recorded at different anode potentials to distinguish between the double layer capacitance caused by the biofilm and that attributable to the electrode.

5.1.1 The capacitance of the anode

EIS measurements were carried out at different applied anode potentials (-0.5 to 0.2 V vs Ag/AgCl). When the results from the anodic impedance measurement are presented as Nyquist plot (Figure 5-2 (b)) two semicircles can be identified. To fit the data a equivalent circuit proposed by (Dominguez-Benetton et al., 2012) was used (see Figure 5-2 (a)), where biofilm resistance and the charge transfer (or polarization) resistance ($R_{CT/P}$), in association with the capacitance of the carbon veil/biofilm and the carbon veil/electrolyte interface were attributed to the two semicircles.

![Diagram](image)

**Figure 5-1:** Equivalent circuit model of the anode (a), Nyquist plot of the anode in a tubular MFC at different applied potential vs Ag/AgCl reference electrode including the fits (b).
As semicircular depression was observed, the capacitance was replaced by a constant phase element (CPE) in the equivalent circuit model and the results for each component, including the corrected capacitance values, are presented in Table 5-1. It can be observed that the first semicircle attributed to the biofilm undergoes only small changes, whereas the second semicircle shows a greater difference with different applied potentials, and also the fit shows a wider deviation from the experimental data.

Table 5-1: Impedance spectroscopy equivalent circuit fitting results for the anode at different applied potentials.

<table>
<thead>
<tr>
<th>Potential vs Ag/AgCl (V)</th>
<th>Current (mA)</th>
<th>1. arc C_{biofilm corr.} (mF)</th>
<th>R_{biofilm} (Ω)</th>
<th>2. arc C_{HL corr.} (F)</th>
<th>R_{CT} (Ω)</th>
<th>χ^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.5</td>
<td>0</td>
<td>8.29</td>
<td>0.916</td>
<td>0.106 - 0.11</td>
<td>53.8</td>
<td>0.0042</td>
</tr>
<tr>
<td>-0.45</td>
<td>0.03</td>
<td>8.49</td>
<td>0.916</td>
<td>0.147</td>
<td>31.1</td>
<td>0.0035</td>
</tr>
<tr>
<td>-0.4</td>
<td>2.46</td>
<td>8.46</td>
<td>0.937</td>
<td>0.148</td>
<td>15.7</td>
<td>0.0007</td>
</tr>
<tr>
<td>-0.3</td>
<td>6.28</td>
<td>8.48</td>
<td>0.929</td>
<td>0.187</td>
<td>26.1</td>
<td>0.0017</td>
</tr>
<tr>
<td>-0.2</td>
<td>6.84</td>
<td>8.71</td>
<td>0.950</td>
<td>0.12*</td>
<td>44.2</td>
<td>0.005</td>
</tr>
<tr>
<td>-0.1</td>
<td>6.49</td>
<td>8.90</td>
<td>0.954</td>
<td>0.148</td>
<td>35.1</td>
<td>0.0041</td>
</tr>
<tr>
<td>0</td>
<td>6.02</td>
<td>8.84</td>
<td>0.971</td>
<td>0.151</td>
<td>35.7</td>
<td>0.0028</td>
</tr>
<tr>
<td>0.1</td>
<td>5.70</td>
<td>8.59</td>
<td>0.996</td>
<td>0.150</td>
<td>36.2</td>
<td>0.0022</td>
</tr>
<tr>
<td>0.2</td>
<td>5.78</td>
<td>8.21</td>
<td>1.029</td>
<td>0.178</td>
<td>36.9</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

\[ Z_{CPE} = \frac{1}{Q(j\omega)^{\alpha}} \] with \( j^2 = -1 \) and \( \omega = 2\pi f \), where \( Q = |Z| \) at \( \omega = 1 \text{ rad s}^{-1} \).

\[ C_{HL} = Q x \frac{x_{\text{max}}^{(\alpha)}}{w_{\text{max}}} \] with \( \chi^2 \) is a measure of the fit quality.

* the Q value wasn’t corrected as \( w_{\text{max}} \) was not available from EIS in the applied frequency range.

As can be seen from Table 5-1, the biofilm resistance increases slightly by up to 12% with increasing anode potentials, ranging from OCP -0.5 to +0.2 V. The double layer capacitance associated with the biofilm varied between 8.2 and 8.9 mF and reached a maximum at -0.1 V vs Ag/AgCl. A significantly higher capacitance of between 147-187 mF was identified by model fitting, for the capacitance of the Helmholtz layer. The capacitance at the electrode/electrolyte interface is therefore 10-20 times greater than the capacitance of the biofilm. In general, there is no clear correlation between the anode potential and any of the capacitance values (\( C_{HL \text{ corr}} \) and \( C_{biofilm} \)), which might be influenced by factors such as temperature or ion concentration. In general the ratio between the Helmholtz layer and the biofilm capacitance will depend on the active surface morphology and biofilm composition and thickness. Hence there is potential to increase both \( C_{HL} \) and \( C_{biofilm} \) by modifying the surface of the electrode material.
5. Duty cycling to enhance power quality in tubular MFC

Figure 5-2 shows the correlation between the different applied anode potentials and the current measured. It can be observed that the current increases with increasing anode potential until it reaches a maximum of 6.84 mA at -0.2 V. Further increases in anode potential do not increase the current, but current remains above 5.7 mA. The polarisation reaches its minimum at -0.4 V with a low current flow.

![Graph showing current and polarization resistance](image)

**Figure 5-2**: Current and polarization resistance, obtained from EIS equivalent circuit fitting at different applied anode potentials vs Ag/AgCl ref (-0.5 V (OCP) to +0.20 V).

5.1.2 Effect of load on the charge accumulation in a tubular MFC

The capacitive property of a tubular MFC operating with a mixed culture biofilm is considered here by calculating the additional charge and simultaneous gain of energy over and above comparative steady state electrical load conditions. The additional charge/energy accumulated during different and prolonged OC times (ranging from 1 to 120 min) and released when connected to loads (ranging between 100 Ω and 3 kΩ) can be seen in Figure 5-3. A clear trend can be observed in the figures as both parameters (charge and energy) significantly increase with decreasing resistance and longer OC times. The lowest resistance (R=100 Ω), which matches the internal resistance of the tubular MFC reactor, resulted in the highest additional charge obtained. After an OC time of 120 min the additional charge was 1.5 C and the additional energy 0.603 J, which is significantly higher than that observed after an OC time of 1 min (0.01 C and 0.004 J). The use of a higher external load resulted in a lower charge accumulation, even though the accumulation period (OC) was the same. Compared to the 1.05 C of extra charge observed at R=100 Ω and t_∞ = 120 min, 0.072 C, 0.031 C and 0.006 C of extra charge were released.
with higher loads of 500 Ω, 1 kΩ and 3 kΩ, which is more than 14, 30 and 160 times smaller, respectively. Hence the evidence shows that the external load influences the additional energy, which is likely to be due to the rate at which the accumulated charge is released during discharging.

![Diagram showing additional charge and energy](image)

Figure 5-3: Additional charge (a) and additional energy (b) obtained with different loads (100, 500, 1 k and 3 kΩ) while varying open circuit periods (1, 2, 5, 10, 20, 60 and 120 min). Note that the charge and energy are ‘additional’ values compared to steady state operation (peak as illustrated in Figure 3-10 over the period between t₁ to t₂).

A smaller external resistance causes a faster charge release and therefore higher current density. At higher loads (500-3000 Ω), the cell potential is close to the open circuit potential, which causes only a small current to flow (0.87-0.18 mA) compared to the steady state current under 100 Ω loading, (i.e. 2.8 mA). It can be seen that depending on
the load, saturation of additional charge accumulation can be observed, which is reached more rapidly the higher the load resistance. This shows the importance of the external load in maximizing the additional charge from the tubular MFC system. The external load clearly regulates the additional energy obtained during the CC-period after OC-operation.

5.1.3 The dynamic response of a tubular MFC to discontinuous operation at different loads

Figure 5-4 (a) shows the influence of different external loads on the cell’s dynamic response, including the separate response of the anode and electrolyte/cathode, before during and after 60 min in open circuit. Figure 5-4 (d) shows the associated current response after 60 min open circuit.

Figure 5-4: Cell, anodic and cathodic potential development (a) before, during and after 60 min charging under 100, 500, 1 k and 3 kΩ, (b) magnification of the anodic potential development, (c) illustration about the losses during OC and (d) the cell current response after 60 min OC at different loads.

The steady state current production was interrupted for 60 min and then reconnected to the load. As opposed to previous studies (Deeke et al., 2012, Bonanni et al., 2012, Uría et
al., 2011, Schrott et al., 2011), where only the anodic capacitance was considered, this experiment focuses on the whole cell, which is closer to real world application and takes the interaction between anode and cathode into account.

It can be seen in Figure 5-4 (b), that the anodic cell potential undergoes relatively small changes in the cell potential of less than 30 mV, when switched from open circuit to closed circuit conditions, whereas the cathodic response is quite similar to the cell response. This might be a consequence of the position of the Ag/AgCl reference electrode, which was situated close to the anode. It also indicates that the cathode is the current limiting electrode, as has been observed in previous studies on tubular reactors with membrane electrode assembly (MEA) (Kim et al., 2011a, Kim et al., 2009). The polarization curve in Figure 5-5 shows similar results and reinforces the assumption that the cathode is the limiting sub-system. It can be seen that the kinetic losses are especially pronounced on the cathode, whereas the anode potential only shows small changes in potential and significantly lower activation losses. The measured open circuit voltage of the reactor is around 0.6 V, which is comprised of a cathode potential of 0.1 V and anode potential of -0.5 V vs Ag/AgCl. It can be seen that the cell potential does not immediately switch to its ultimate open circuit potential, furthermore a rapid change, within a few seconds can be observed initially, followed by a monotonically decreasing rate of change which occurs over a longer period, until ultimately open circuit potential is reached.

Figure 5-4 (c) explains the origin of the potential development if switched from closed circuit to open circuit operation and the subsequent transient state. The first drop in potential is associated with the rapid recovery from the ohmic losses, which include the resistance of the biofilm, the membrane and the electrolyte resistance. This component is more pronounced in the cathode associated data due to the reference electrode positioning in the proximity of the anode (2 mm) as mentioned in section 3.8.3; hence most of the anolyte resistance and the membrane resistance are apparent in the cathode data. The reactor configuration (cathode/membrane assembly) makes it impossible to record the cathode potential independently of the voltage drops caused by the components between the cathode and the reference electrode. The monotonic rise with diminishing rate, which follows the recovery from the ohmic losses, is caused by the progressive diminution of the activation losses. After that the potential slowly approaches the final OCV. The activation losses are associated with the capacitive double layer charge
formation and dissipation, as once the cell is in open circuit it requires time to reach the final polarized equilibrium state.

Figure 5-4 (a) shows that the time required to achieve the open circuit equilibrium state will depend on the external load resistor. If 3 kΩ were to be used as an external resistor the OCV was achieved within 60 min, as can be seen in Figure 5-4 (a). The final equilibrium OCV was not reached within an hour if external loads of 1 kΩ, 500 Ω and 100 Ω were used, as the double layer capacitance takes a longer time to dissipate its charge and reach the final equilibrium. The saturation type characteristic observed for 3 kΩ in Figure 5-3 occurs as a result of the fact that the equilibrium open circuit potential was already reached within 60 min, hence no increase in the additional charge was observed if the OC-time was prolonged to 120 min. The potentials measured after 60 min in open circuit were 536 mV, 560 mV, 592 mV and 597 mV for R=100 Ω, 500 Ω, 1000 Ω and 3000 Ω, respectively; showing that the higher the resistance the closer the open circuit potential to the final OCV value (after tOC=60 min).

Figure 5-4 (c) focuses on the anodic potential changes which occur when the reactor is disconnected for 60 min from the different loads (OC-operation) and then after reconnection (CC-operation). During OC the anode potentials are almost equal and only under R = 100 Ω there is a slightly higher anode potential observed. Also, the difference between the anodic potential in CC- and OC-operation is only 20 to 30 mV, regardless of the load.

After sudden reconnection to a load, a peak is observed in the potential, which is attributed to the double layer capacitance and the rapid decrease in non-faradaic current. The faradaic component is believed to derive from electron exchange between the bacteria and the electrode. It can be seen that under R=100 Ω loading, the peak observed after reconnection only approaches the final equilibrium after 20 min. Hence for 20 min a slightly higher anode potential is observed, which is beneficial to the bacteria and can enhance electron discharge from the electrogenic biofilm to the anode.
5. Duty cycling to enhance power quality in tubular MFC

Figure 5-5: Polarization curves for the tubular MFC and their anodic and cathodic component vs a Ag/AgCl reference electrode situated next to the anode as well as the resulting power curve.

5.1.4 The influence of short open and closed circuit times on the average current, average power and energy efficiency

As described in section 3.8.3.3, an automated OC/CC mechanism was applied to the MFC with shorter open and closed circuit intervals than presented above. The results obtained from OC-times ≤ 10 s and CC-times ≤ 300 s in terms of average power and current with and without consideration of the OC times, are presented in Figure 5-6. It can be seen that the average currents and powers differ largely dependent on the reference period. Hence if only the CC period is considered (dashed lines) the average current/power is always higher than under the same load in continuous steady state operation (ranging between $I_{ss} = 2.46-2.67$ mA; $P_{ss} = 0.61-0.72$ mW, indicated by the grey area in Figure 5-6 (a) and (b). However, the opposite can be observed if the entire OC/CC period is used as reference periods (solid line), i.e. the current/power is always lower than under the same load in continuous steady state operation. Hence, if the current or power is averaged over an entire OC/CC cycle, short OC (up to 10 s) and long CC-periods (60 s) result in low current/power gains, which are comparable to the values obtained in steady state operation.
5. Duty cycling to enhance power quality in tubular MFC

Figure 5-6: The effect of automated short on/off cycling on average power production according to various OC- and CC- times (OC = 0.5-10 s; CC = 1-300 s). The external resistance was 100 Ω: (a) average power generation, (b) average current. The dashed lines represent the averaged value over only the CC-period, and the solid lines indicate the averaged value over the entire OC/CC-cycle period (Error bars represent standard deviations based on four different cycles).

It is clear that the system would normally operate continuously, hence the total OC/CC period would seem to be the most appropriate comparative measure. Nevertheless, if the parameters are only averaged over the CC period the highest values in terms of average power and current were obtained with t_{cc} = 1 s. In combination with an OC-period of 10 s, an average current of 4.0 mA and a greater than 2-fold increase in average power (1.32 mW) than under steady state operation can be achieved. Short discharge periods especially, can enhance the average power and current, as the current decay is interrupted before reaching the stable baseline. The results indicate that the initial peak voltage can be further increased by adjusting open and closed circuit periods; hence
longer open- and shorter closed circuit periods can increase the averaged values for power and current.

Figure 5-7: Switched mode energy efficiency (SMEE) during automated OC/CC operation (Error bars represent standard deviations based on four different cycles).

Figure 5-7 shows the switched mode energy efficiency (SMEE), which compares the energy produced during discontinuous operation with the energy produced during continuous operation at steady state under a constant load $R = 100 \, \Omega$. The overall energy efficiency decreases with increasing average power and current output when only CC is considered, and high energy efficiencies (90-99%) are achieved with prolonged discharge periods of 60 s and 300 s, which results in less improvement in power quality and indicates that prolonged CC periods might offset the effect of cycling. However, short OC/CC cycling resulted in higher average current and power over the CC time but this occurs at efficiencies well below 100%; for example 4.1 mA and 1.3 mW produced at 10s-OC/1s-CC operation delivered only 19% SMEE. Nevertheless it is important to note, that the parameter SMEE doesn’t provide information on the usability of the generated power.
5.1.5 The influence of open circuit time and load on the maximum voltage gain

Figure 5-8 shows the maximum voltage gain after prolonged OC-times ranging between 1 and 120 minutes, at different loads (100-3000 Ω) (a); and after short OC-periods of between 0.5 and 10 seconds with OC/CC operation (b). The maximum voltage increase at 100 Ω over continuous steady state operation rose from 30 mV to 150 mV, after open circuit times of 1 to 120 minutes and decreases at higher loads to 40-114 mV (500 Ω), 22-104 mV (1000 Ω) and 8-65 mV (3000 Ω), after OC times of 1 to 120 min respectively. Hence the higher potential immediately after OC operation is significant, considering the cell potential of between 250 and 280 mV under 100 Ω. The voltage increase with short and prolonged open circuit times is attributed to the pseudo-capacitance, however, the contribution of the double layer capacitance seems to increase the voltage especially at short OC/CC-cycling.

Figure 5-8: Maximum voltage gain after (a) long OC-periods (1-120 min) at different loads (100-3000 Ω) and after (b) short OC-periods (0.5-10 s) at automatic CC/OC operation (R=100 Ω).
Comparably significant voltage increases were observed during the discontinuous (switching) mode, where OC-periods of only 0.5-10 s had already resulted in voltage increases of between 45-125 mV (see Figure 5-8 (b)). Also noteworthy is the linear relationship between OC-time and maximum voltage observed during short automatic OC/CC operation. The deviation of the linear relationship at \( t_{oc} = 0.5 \) s might have derived from resolution limitations at shorter time intervals and the detail of the virtual instrumentation and used National Instrument card. These results indicate, that the desired effects of the double layer capacitance, benefits from rapid switching in particular and accounts for the improved power quality.

### 5.2 Discussion

The results imply that the high surface area of the carbon veil anode with an electrochemically active biofilm, exhibits a relatively high capacitive behavior which can be used to enhance the power quality in MFCs. The effect, which enhances the usability of the power derives from a \textit{pseudo}-capacitance, which is composed of a non-faradaic current derived from the double layer capacitance and a faradaic capacitance. The faradaic component derives from the biofilm, manifest by the electron transfer to the anode; hence involves an electron transfer. The non-faradaic current derives from charge separation between the electrolyte/biofilm/electrolyte and the electrolyte/membrane/electrode interface. In this study a mixed culture biofilm was used to investigate the \textit{pseudo}-capacitance and investigates the practical application of these phenomena. Pure culture studies have been carried out (Uría et al., 2011, Bonanni et al., 2012, Schrott et al., 2011), considering the underlying mechanism. However, no quantification or relation between the faradaic and non-faradaic current has been given. As in this study a mixed culture biofilm was used, hence the capacitance is a combination of several mechanisms such as charge storage in cytochromes, mediators, metabolites and electron transfer to the anode during open circuit operation. In an abiotic experiment, an attempt was made to set the anodic potential vs Ag/AgCl to imitate the conditions; it was not possible to stabilize the potential to the set conditions. The results obtained from fitting the equivalent circuit to the anode spectra to try to distinguish between the double layer capacitance of the biofilm/electrode and electrolyte/electrode, indicate it is not possible to adequately distinguish between the faradaic and non-faradaic components, which are also expected to depend on the anode potential.
5.2.1 Additional charge accumulation during open circuit operation

With respect of the additional charge accumulation during open circuit operation and discharge (CC) under different loads, it was shown that the magnitude of the load is of importance. A lower external resistance causes a more rapid charge accumulation and release, thus obtaining higher current densities. Higher loads (500-3 kΩ) resulted in less charge accumulation during OC and caused only a small current to flow (0.87-0.18 mA) compared to the steady state current under 100 Ω (2.8 mA), because the difference between the cell potential under a load and the open circuit potential is small. Hence the selection of external resistance is of importance in maximizing the additional energy accumulated with respect to longer charging time (i.e. OC-period).

5.2.2 Short OC/CC cycling to improve the power quality

MFCs produce low quality power in terms of their applicability as direct power supply. The low quality of power produced from MFCs makes it difficult to operate commonly available low power consuming electronic devices (include biosensor, microprocessors of operational amplifiers). One plausible approach would be to boost the voltage and power instantaneously with discontinuous OC/CC operation provided that the MFC exhibits a sufficiently high internal capacitance in the MFC.

In order to investigate the effect of more rapid OC/CC-cycling on the power output, an automated on/off mechanism was developed and applied to the tubular MFCs. This mode of operation was tested to define the extent to which it can increase the quality and therefore the utility of the power produced. As power quality was improved, such rapid cycling might act alone, or in combination with other sources to supply power for low energy consuming devices.

The energy efficiency was clearly shown to be lower under discontinuous operation; hence the intrinsic capacitance can increase the power quality but only at the expense of energy efficiency. In this context it has to be kept in mind, that other methods to increase the power exist, such as DC/DC converters which will have conversion efficiencies of 70-95% (Erikson, 2013). The energy losses from such OC/CC switching may be tolerable if the power is aggregated over many MFC modules with an appropriate module connection strategy. So alternating switching between the modules might produce a continuous...
5. Duty cycling to enhance power quality in tubular MFC

power supply with sufficient potential. The lower energy efficiency due to the OC/CC cycling might be a problem in high power producing conversion equipment such as PEM fuel cells using a costly hydrogen fuel. However, an operational strategy that increases quality of power at the expense of energy efficiency might be advantageous in biological fuel cells, which may use inexpensive and abundant biodegradable substrates such as wastewater. Further developments in tailored OC/CC operating strategies may increase power quality and reduce the efficiency loss from MFC systems. Thus this OC/CC cycling strategy for power quality improvement might contribute to the applicability of bioelectrochemical processes.

5.2.3 Non-faradaic component

Previous studies have investigated internal capacitance in half cell conditions (Sevda et al., 2014b, Deeke et al., 2012, Bonanni et al., 2012, Uría et al., 2011, Schrott et al., 2011). This study uses a carbon veil anode with relatively high specific surface area with a biofilm and a membrane cathode assembly to enhance double layer capacitance. As opposed to the other studies, this experiment takes the interaction between anode and cathode into account and considers the potential development across the whole cell under varying operating condition.

Electrochemical impedance analysis was carried out in association with equivalent circuit modeling to distinguish between the capacitance of the biofilm and the Helmholtz layer, due to charged and polar components present in the anolyte. The latter was found to be relatively insensitive to different anode potentials. Also, the biofilm itself exhibits a double layer capacitance, which derives from extracellular components such as metabolites and physical appendages or pili of the bacteria (Kim et al., 2011b). Aggregating both components (\(C_{\text{biofilm}} + C_{\text{HL}}\)), results in a capacitance of 114-196 mF at the range of potentials applied and therefore contributed significantly to MFC’s capacitance (see table Table 5-1). It can be estimated that the specific capacitance is approximately 650 mF l\(^{-1}\) based on reactor liquid volume (or 0.151 mF cm\(^{-2}\) based on total area of carbon veil electrode surface, 1035 cm\(^2\); 12.07 mF cm\(^{-2}\) for the projected surface area of 13 cm\(^2\)). The carbon veil anode exhibits a high surface area and enables the accumulation of a double layer charge at the hybrid carbon veil/electrolyte/biofilm interfaces.
In general the double layer capacitance was found to be dependent on the electrode material and its specific surface area. Kim et al. (2011b) investigated *Pseudomonas aeruginosa* PA14 and found a decreased capacitance from the presence of a biofilm, which varies slightly with the culture, whereas Manohar et al., (2008b) observed no influence from a *Shewanella oneidensis* biofilm.

Not only the anode but also the cathode exhibited capacitive behavior. Manohar et al., (2008b) reported that the double layer capacitance of the cathode was two orders of magnitude higher ($10^{-4}$ F to $10^{-2}$ F) when graphite felt electrodes with a surface area of 20 cm² were used. They suggested that this was caused by the higher specific surface area due to the Pt-layer. Zhao et al. (2009) used BET analysis to measure the specific surface area of carbon fiber veil and activated carbon cloth, which revealed that the specific surface area of carbon fibre veil was significantly lower ($<0.3 \text{ m}^2\text{g}^{-1}$) than activated carbon cloth measuring 1038 m²g⁻¹. In the tubular reactor reported here the cathode was attached to a CEM. Hence a charged double layer is built up on the cathode surface as well as on the membrane surface, both contributing to the cathodic capacitance effect.

It was observed that when the system is switched from open circuit to closed circuit the anode potential moves slowly but characteristically toward the final equilibrium potential (OCV). Even though the difference between the initial drop in potential when switched to OC potential and the final OCV is small, the electrogenic bacteria are able to use the electrode as final electron acceptor to the point that the final OCV is reached; hence beyond closed circuit electron accepting condition. The electrons can be stored in the anode during the open circuit period and released when the circuit is closed. Deeke et al. (2012) have modified a graphite plate anode with activated carbon powder and a N-methyl-2-pyrrolidone and Polyvinylidenfluoride containing polymer solution and compared the capacitance to the non-modified electrode. Due to the modification, the anode potential was kept higher for longer during open circuit than the anodic potential of the non-modified electrode and more electrons were accepted from the biofilm during OC. The cumulative total charge after 15 cycles at $t_{oc} = 5$ min and $t_{cc} = 20$ min increased from 12 195 C m⁻² (unmodified) up to 22 831 C m⁻² (modified) at a set anode potential of -0.3 V vs Ag/AgCl. In our reactor the same OC/CC cycles resulted in a 74% higher cumulative charge of 39,807 C m⁻² (at R=100 Ω) after 15 cycles and a projected outer anode surface area of 13 cm² as a reference. In a tubular MFC, the biofilm was found to be mainly present on the outer layer of the carbon; the biomass concentration was found to
be significantly lower, most likely due to mass transfer limitations in the inner layers (Kim et al., 2009, Michie, 2012). Thus it was decided to use the projected outer anode surface area of 13 cm$^2$ as a reference.

The mixed culture biofilm used in this study consists of strains capable of direct electron transfer such as *Geobacter sulfurreducens* and *Shewanella oneidensis*, which were both found to be able to accumulate/store charge in their outer membrane cytochromes (Schrott et al., 2011, Uría et al., 2011, Esteve-Núñez et al., 2008, Summers et al., 2010). Schrott et al. (2011) investigated the charge accumulation of *Geobacter* biofilms on graphite bars with 8 cm$^2$ surface area. Despite the findings, that the additional charge increased with increasingly positive anode potential, a poised anode potential of $+0.4$ V vs. NHE, resulted in two orders of magnitude smaller excess charge after OC=10 min, than the excess charge in the tubular reactor as can be seen in Figure 5-3 (6.25 x 10$^{-4}$ C compared to 6.27 x 10$^{-2}$ C at $R=100 \ \Omega$, $A=13 \ cm^2$). Hence the double layer capacitance on the electrolyte/biofilm/electrode interface was significantly improved. However, not only species capable of direct electron transfer, but also strains which produce mediators to transfer electrons to the anode are present, which can also store electrons under open circuit. Zhao et al. (2009) investigated a *Desulfovibrio desulfuricans* biofilm for sulfite and thiosulfate reduction. This study showed that the sulfide metabolite concentration affected the anode potential.

In Figure 5-9 (b) the anodic discharge characteristic shows a prolonged discharge time of 20 min before steady state was reached. The observed peak could result from changes of the redox state of certain outer membrane cytochromes known to be involved in the electron transfer, such as *OmcS* and *OmcZ*. Those membrane cytochromes can accumulate the electrons during open circuit (reduced state) and release electrons once the electrode is available as electron acceptor during closed circuit (oxidizing state). A study by Bonanni et al. (2012) has found that such rapid release of charge induces a potential gradient in the biofilm, which enhances the charge transport through the bacteria in the biofilm. This facilitated charge transfer might explain the anodic peak potential at 70 min which could originate from the rapid release of stored electrons by the oxidation of the cytochromes (Figure 5-10 (b)). Only a very recent study by (Sevda et al., 2014a) has investigated the anode and cathode capacitance (activated carbon cloth anode and activated carbon – VITO cathode). This study has shown that the anode potential reached its equilibrium notably 20 min after being reconnected to $R=1480 \ \Omega$. However, their study showed a
more significant change in the anodic potential when switched from closed to open circuit conditions, which was also found to depend on the external load. The anode potential was around -5 to 10 mV vs Ag/AgCl during CC but dropped significantly to -340 to 420 mV vs Ag/AgCl after 70 min in open circuit. The reason why such significant changes were not observed in the case reported here might be due to the cathodic limitations mentioned above. In general the anode potential is determined by the ratio of oxidized to reduced extracellular membrane cytochromes, hence once the cytochromes get oxidized and transfer the electrons to the anode, a more positive anode potential can be observed (CC).

5.3 Conclusions

This study showed that a tubular MFC with an acclimated mixed culture biofilm on a high surface area carbon veil electrode exhibits a significant pseudo-capacitive behavior, which can be used to increase the usability of the power produced. The double layer capacitance investigated by EIS, showed that the capacitance ascribed to the biofilm was more than one order of magnitude smaller than that of the Helmholtz layer associated capacitance. The pseudo-capacitance consists of a non-faradaic component along with the charge storage capability of the carbon veil and electrogenic biofilm. Periodic open and closed circuit operation can be used to increase the quality or usability, but only on the expense of energy efficiency. The OC/CC switching mechanism might enable sufficiently increased voltage to supply low power electronic devices without altering the system components or configuration (i.e. electrode material, catalyst, binder etc) and the need for external boosting mechanisms such as external capacitors.
6 Catalyst and binder materials for oxygen reduction reaction in Microbial fuel cells

This section presents the experiments carried out to identify new binder/catalyst combination to enhance the oxygen reduction reaction. Due to the high overpotential of the ORR, new materials have to be tested regarding their catalytic property and cathodic activation losses. The main focus of this study lies in the binder materials and their interactions with the catalyst, which governs the activity. Hence, this chapter presents results of different binder materials including ILs and their influence on the Pt- and FePc catalyst performance. On the basis of these results, an alternative catalyst/binder system to the commonly used Pt/Nafion system should be identified.

6.1 Results

Linear sweep voltammetry and cyclic voltammetry were measured in half cell conditions as presented in section 3.8.2. Different carbon paste electrodes with different binders and carbon ratios on carbon paper as the base materials were tested. The first results presented (section 6.1.1) are based on activated carbon (AC) with different binders, including a conductive IL [BuMeIm]⁺ [PF6]⁻ and a proton conductive IL [empa]⁺ [NfO]⁻, designated in the figures as BMIM and EMPA, respectively. These IL based binders were compared with the commonly used binders Nafion and PTFE. In the next experimental section (section 6.1.2) the binders were used in combination with Pt and FePc to test their catalytic properties when used in combination with the ILs.

Both ionic liquids are relatively hydrophobic, especially due to the fluorinated anions hexafluorophosphate [PF6]⁻ and nanofluoromethansulfonate [NfO]⁻. The cations [BuMeIm]⁺ and [empa]⁺ are more hydrophilic, where latter exhibit a proton exchange functional group (R-NH₄⁺).
6.1.1 Carbon paste electrodes with Activated carbon and Ionic liquids as binders

Experiments were conducted with Activated Carbon (Norit, SXRO PLUS, Amersfoort, Netherlands) as carbon base material in combination with two ionic liquid binders. In order to see the effect of heat treatment, the electrodes were either dried at room temperature or at 110 °C. Figure 6-1 presents the linear sweep voltammetry results obtained from abiotic cathodes.

The results indicate that drying the carbon paste electrodes at elevated temperature is not beneficial for the current production. The reduction current was highest for the activated carbon/[BuMelm]⁺[PF6]⁻ electrode dried at ambient temperature and was significantly lower when heat treated. The difference was less pronounced when AC was used in combination with [empa]⁺[NfO]⁻.

![Figure 6-1: LSV of Activated carbon/ionic liquid carbon paste electrodes with heat treatment (heat) and without heat treatment (RT).](image)

The AC/IL paste was found to be too brittle and due to shear stresses during the measurement the paste detached from the carbon paper support, partially dissolved in the electrolyte (50 mM PBS). Hence pure activated carbon suspended in the binder was not found to be appropriate in terms of long term operation. In the next step the activated carbon was mixed with carbon black to improve the stability of the paste produced.
Figure 6-2 presents the results of LSV of several carbon pasted electrodes made from activated carbon and carbon black in combination with Nafion and IL as a mixed binder. The legend provides details of the composition (AC, CB, binder) and amount (mg or µl). Additionally, a plain carbon paper electrode was measured for comparison purposes. It was observed that the paste became more stable after the addition of carbon black. The carbon paste electrode (1) made from 50 mg AC, 30 mg CB electrode (AC/CB ratio of 1.6) and 400 µl Nafion resulted in the highest current. When the Nafion content (400 µl) stays the same and the amount of AC is increased to a AC/CB ratio of 5 (see electrode 5) the performance in terms of the current density stays the same than for electrode (1) until a potential of -0.2 vs Ag/AgCl is reached, from which point onwards the current density is found to be lower. When 100 mg AC are mixed with 400 µl Nafion (electrode 4) the paste is again found to lack mechanical stability and this arrangement also resulted in lower current densities.

A AC/CB ratio of 1.6, while replacing 50% of Nafion content with either [BuMeIm][PF6] (electrode 2) or the proton conductive IL [empa][NfO] (electrode 3) resulted in a significantly lower current density than with 100% Nafion. Out of the two tested ILs [empa][NfO] achieved higher current densities. A mixture of both IL in the ratio 1:1 (electrode 6) resulted in a similar potential/current profile to electrode 2.
Cyclic voltammograms of the same electrodes presented in Figure 6-2, conducted at different scan rates (5, 20 and 50 mV s\(^{-1}\)), are shown in Figure 6-3. It can be seen that no clear reduction peak can be observed. The use of Ionic liquids as binders resulted in relatively flat cyclic voltammograms. This is especially the case for electrode 5 which uses a mixture of both ionic liquids. The brittle electrodes with high concentrations of activated carbon content (electrodes 4 and 5), resulted in the highest reduction current density at low potentials (see Figure 6-3 (a)). At higher scan rates of 20 and 50 mV s\(^{-1}\), electrodes 1 and 5 resulted in a higher current, indicating a higher capacitance.

![Cyclic voltammograms at different scan rates](image)

Figure 6-3: CVs at different scan rates of Activated Carbon paste electrodes with different binders.
6.1.2 FePc and Pt based carbon paste electrodes with different binders

Carbon/catalyst pasted electrodes were prepared using two different catalyst (2 mg cm\(^{-2}\) FePc and 0.5 mg cm\(^{-2}\) Pt) and selected binders. In this case different amounts (120 and 180 µl) of ILs ([BuMeIm]\(^+\) [PF6]\(^-\) and [empa]\(^+\) [NfO]) were tested to observe changes in the reduction current (see Figure 6-4). If the LSV results from the FePc based carbon paste electrodes are compared to the Pt based electrodes (see Figure 6-4), it can be observed that the FePc based electrodes undergo oxidation, as a clear oxidation peak can be observed between 0.25 and 0.35 V vs Ag/AgCl. Furthermore it can be seen that the Pt based electrodes give a reduction current at more positive potentials of up to 0.22 V vs Ag/AgCl, which is desirable when seeking to achieve higher cell potentials in the MFC.

Figure 6-4: LSV of carbon paste electrodes based on 2 mg cm\(^{-2}\) FePc and 0.5 mg cm\(^{-2}\) Pt with Nafion, PTFE and 120 or 180 µl of the ILs [BuMeIm]\(^+\) [PF6]\(^-\) and [empa]\(^+\) [NfO].
The current of all Pt based electrodes goes through zero at a common potential (0.22 V) from here on, a positive oxidation current is produced (Figure 6-4 b). The FePc based electrodes (Figure 6-4 a) show a different behavior and depending on the binder, the reduction current is limited to a lower potential than the Pt based electrodes.

Both figures (Figure 6-4 (a) and (b)) contain the Linear Sweep Voltammograms of a commercial 10% Pt carbon paper electrode (Fuel cell earth, Wakefield), which resulted in the highest reduction current density. The LSVs indicate that the performance of FePc and Pt depends on the binder. When 0.5 mg cm\(^{-2}\) Pt was used as a catalyst the proton conductive IL [empa\(^+\) [NfO\(^-\)] (120 µl) resulted in the highest current density after the commercial Pt electrode. Also it was observed that the lower amount of IL (binder loading) of 120 µl resulted in higher current densities than with 180 µl. In the case of FePc used as catalyst, the different amounts of binder (ILs) had only a small impact on the current density. In general the Pt based electrodes show a higher current density than when FePc was used as the catalyst. The Pt based electrodes showed the highest current density with [empa\(^+\)][NfO\(^-\)] as binder, followed by Nafion and [BuMelm\(^+\)][PF6\(^-\)], which showed a similar current density/potential profile. The Pt-IL based carbon paste electrodes resulted in a higher reduction current than the common binders Nafion and PTFE. Pt catalyzed electrodes based with Nafion as binder, resulted in the lowest current density. The opposite was observed with FePc catalysts which obtained the highest current density with the PTFE binders.

Figure 6-5 shows CVs of carbon paste electrodes with either Pt or FePc with Nafion, PTFE and the ILs [empa\(^+\)][NfO\(^-\)] and [BuMelm\(^+\)][PF6\(^-\)] at three different scan rates (5, 20 and 50 mV s\(^{-1}\)). In contrast to what was observed in Figure 6-4 in the LSV (v=1 mV s\(^{-1}\)) the CVs at v=5 mV s\(^{-1}\) (see Figure 6-5 (a) and (d)) resulted in a higher current from electrodes using FePc catalyst. Also at higher scan rates of v=20 mV s\(^{-1}\), the FePc catalyzed electrodes resulted in a higher current and when the scan rate increased to 50 mV s\(^{-1}\) the difference in current between the two electrodes was reduced. This may indicate that electrodes prepared with a FePc catalyst loading of 2 mg cm\(^{-2}\) presented a higher capacitance. The commercial 10% Pt carbon paper electrode resulted in a broad reduction peak having its maximum at ~0.2 V vs Ag/AgCl, whereas the carbon paste electrodes prepared with Pt exhibited a small reduction peak at 0.0 V vs Ag/AgCl. A broader peak, but in the same potential range, can be observed from the FePc based electrodes at v=5 mV s\(^{-1}\) (see Figure 6-5 (d)). Similarly to the LSVs an oxidation peak can be observed for the FePc catalyst in
combination with IL based binder. The reduction and oxidation peaks become less pronounced with increasing scan rate. In both cases (Figure 6-5 (a) and (d)) the IL based carbon paste electrodes resulted in a higher peak reduction/oxidation current at \( V = +0.6 \text{ V vs Ag/AgCl} \), likely indicating a higher double layer capacitance.

Figure 6-5: Cyclic voltammograms at different scan rates of carbon paste electrodes based on 2 mg cm\(^{-2}\) FePc and 0.5 mg cm\(^{-2}\) Pt with Nafion, PTFE and 120 or 180 µl of the ILs [BuMeIm]\(^+\) [PF6]\(^-\) and [empa]\(^+\) [NfO].
6.2 Discussion

The work presented in this chapter represents a study on different catalyst/binder systems, to identify an alternative to the Pt/Nafion system currently used, with a higher performance/cost ratio. For the first time ILs were tested as potential binder materials in MFCs cathode and compared to commonly used Nafion and PTFE binder. The interaction between the binder material and the catalyst was investigated in terms of their current response to an applied potential range. The carbon paste electrodes based on new binders and FePc or Pt as a catalyst were tested in half cell conditions. On the basis of these results, a cheaper alternative to the commonly used Pt/Nafion system was sought to reduce the capital costs of a scaled up reactor.

6.2.1 Carbon paste electrodes with AC and ionic liquids as binder

The first results presented in section 6.1.1 with Activated Carbon indicate that mechanical instability is prevalent when paste is applied with only AC mixed with the binder. Zhang et al. (2014b) have also found that blending AC with carbon black will increase the performance. Different ratios of CB:AC (0, 2, 5, 10 and 15 wt%) have been tested and it was found that the addition of 10 wt% carbon black increased the power density. In the presented study the addition of CB was necessary to produce a stable paste. The addition of 38 wt% CB resulted in the highest reduction current, followed by 17 wt% CB (see LSV Figure 6-2). Also it has been shown that the performance of AC in terms of the ORR activity is dependent on the precursor material, hence the base material from which the AC was produced. In this study the AC was Norit SXRO PLUS, which is used as a catalyst in herbicide production; however, no indication of the precursor material was discovered. Watson et al. (2013b) have tested AC based on coal, peat, coconut shell, hardwood and phenolic resin and found that the precursor material plays an important role. Coal based AC had the highest power density and acidic surface functional groups were found to have a negative impact on the ORR. In contrast, functionalization with ammonia gas was found to be beneficial, but the increasing basicity has also been shown to increase the adsorption for organic matter which can therefore block the active sites (Watson et al., 2013a). Also Wang et al. (2014) considered the addition of quaternary ammonium or mixing with anion exchange resin to enhance OH⁻ transfer in AC carbon based cathodes. Another recent study increased the performance of AC by pyrolyzing it with FeEDTA, which exhibited a better long term performance as a Pt catalyzed air cathode (Xia et al., 2013). Hence there are
many factors influencing the performance of activated carbon as an oxygen reduction reaction catalyst. In this study an unmodified AC powder was considered, which resulted in lower current densities than carbon paste electrodes with Pt or FePc catalyst (see Figure 6-4).

6.2.2 Influence of the binder on the catalytic activity

In section 6.1.2 Pt and FePc were used as catalysts, exploring different loadings (0.5 mg cm\(^{-2}\) Pt and 2 mg cm\(^{-2}\) FePc) in terms of the ORR. The higher specific loading for FePc may be justified by the significant lower cost; 10 g Pt costs around £979 (Premetek), whereas 10 g FePc costs around £89.4 (Sigma Aldrich). As can be seen from the recorded linear sweep voltammograms, the Pt based electrodes resulted in a higher reduction current. In this study, the iron(II) phthalocyanine (FePc) was ball milled with carbon black before use, but was not pyrolysed, which would have increased its catalytic activity (Birry et al., 2011b). Pyrolysis was omitted as the primary focus of the study was to identify suitable binders in terms of ORR performance and also previous binder focused studies have used unpyrolysed FePc (Yu et al., 2012). Furthermore, to determine if there would be interdependence between the catalyst and binder; i.e. if the types of catalyst and their activities might depend on the type of binder used.

Typical pre-treatments involve mixing the FePc with carbon nanoparticles in tetrahydrofuran THF, followed by heat treatment at 700 °C after removing the solvent (Zhao et al., 2005b, Zhao et al., 2006). In another study by Hao Yu et al. (2007), the FePc powder was dissolved in 98% H\(_2\)SO\(_4\) before the carbon nano particles were added and stirred overnight, filtered washed and dried (110 °C) before pyrolysing at 800 °C in an Argon atmosphere for 2 h. The oxidation current obtained in the LSVs (Figure 6-4) might be due to the non-pyrolysed material used in this study, as pyrolysis would have oxidized all possible extraneous materials and impurities present. Also, it is known that pyrolysis increases the catalytic activity and stability of FePc and can change the reaction mechanism from a two electron to a four electron mechanism (Lee et al., 2009). It was found that Pt produces a reduction current of up to +0.2 V vs Ag/AgCl, whereas the performance of FePc depends on the binder used (+0.1 to 0.25 V vs Ag/AgCl). Similar results were reported by Birry et al. (2011a), as Pt produced a reduction current up to 0.2 V vs SCE and FePc was limited to +0.2 V vs SCE.
Apart from the catalyst and binder material, the cathodic performance in a Microbial fuel cell will also depend on the salinity of the electrolyte. Wang et al. (2011b) has found that the addition of NaCl (to increase the conductivity/salinity) reduced the reduction efficiency of Pt based cathodes but improved the performance of CoTMPP cathodes and similar might be observed with FePc, but was not considered in the author’s study.

### 6.2.3 The performance of Ionic liquids as binder

The binder material plays an important role in the ORR, as it acts on the interface between the gas, electrons, protons and the electrocatalyst. The ideal binder exhibits good proton conductivity and oxygen permeability. Platinum not in contact with binder is usually not electrochemically active (Sambandam and Ramani, 2010). The most common binder material in PEM and microbial fuel cells is Nafion, which exhibits a hydrophobic backbone and a hydrophilic ionic sulphate group for proton conduction, but PTFE is also commonly used in MFCs, which is very hydrophobic without any functional groups. On the one hand hydrophobic binders such as PTFE have good oxygen transfer properties, but are less effective in terms of proton transfer; on the other hand hydrophilic materials are thought to have a higher oxygen solubility through the water uptake, which will enhance the performance (Saito et al., 2011). In this study non-polymeric binders were tested and for the first time ionic liquids were used as binder materials for air-cathodes in MFCs. Both of the tested ILs, [BuMeIm]⁺[PF6]⁻ and [empa]⁺[NfO]⁻ are hydrophilic, which is particularly useful in MFC due to the direct contact between the electrolyte and the binder, which should ensure the stability of the catalyst/electrolyte interface. Another advantage of protic ionic liquid is their antimicrobial activities (Yang-jun et al., 2011). Hence protic IL have the potential to inhibit microbial growth on the cathode, which is known to decrease the long term performance of MFCs.

The carbon paste electrodes prepared with IL-based binders and Pt or FePc separately, are composed of hydrophobic fluorinated anions (hexafluorophosphate and nano fluoromethanesulfonate), which should provide good oxygen diffusion capabilities. The cations are more hydrophilic and in the case of [empa]⁺, it has a proton conductive functional group. Due to the strong Coulombic interactions between the anion and cation components, it can be expected that when used as binder both ionic species will be in close proximity. Theoretically therefore ILs represent an ideal replacement for polymeric binders. In this study no significant improvement was observed with IL binders compared to the
commonly used binders (Nafion, PTFE) in the half cell studies (LSV and CV). It was however shown, that depending on the catalyst, different binder materials result in improved performance. Using LSV, FePc produced the highest current with PTFE as the binder, whereas Pt delivered the highest current density when IL was used as the binder, followed by Nafion. Two different binder amounts were tested for Ionic Liquids (120 and 180 µl) and it was found that in combination with AC carbon and Pt, a lower loading is preferable, while in combination with FePc equal current densities were achieved. Study of a wider range of ionic groups and further optimization of the IL system is needed to increase the catalytic activity. Also, it is worth mentioning that IL binder based carbon paste electrodes exhibit a higher double layer capacitance, as can be seen from the cyclic voltammograms presented in Figure 6-5. This is due to the ionic nature of the ILs, which has been found in several previous studies (Musamah and Wang, 2008, Maleki et al., 2006). The higher capacitance can be of special interest for certain applications such as the work previously introduced in Chapter 5 in relation to duty cycling.

Several studies have tried to identify an ideal binder for MFC, but there is no agreement on the ideal properties in terms of hydrophilicity or hydrophobicity, non-ionic, cationic or anionic functionalization. Some studies found, that non-ionic hydrophobic properties are more beneficial (Saito et al., 2010), whereas another study stated that neutral hydrophilic cathodes are ideal, showing no agreement on either hydrophobic or hydrophilic properties. In opposition to this findings Chen et al. (2012a) reported their highest current with fluorinated quaternary ammonium polymers (ionic); whereas hydrophilic proton conductive EDTA (non-ionic) was used by Gong et al. (2014) and a hydrophilic anionic exchange ionomer was found to perform better as binder than Nafion (Yu et al., 2012).

### 6.3 Conclusion

It has been shown for the first time that IL can be used as a binder material in carbon paste electrodes for ORR. The performance in terms of catalytic activity measured as current density in a LSV half cell study revealed that the binder material should be chosen with consideration to the electro-catalyst (Pt or FePc). Hence the catalytic activity of each catalyst was found to be dependent on the chosen binder material and in the case of Pt, was also a function of the IL-binder loading. However, further experiments need to be carried out to find the optimum catalyst loading. In terms of the catalyst costs, the price of
FePc is significantly (~11 times) lower than Pt and whereas pure Nafion costs 61.3 £ ml$^{-1}$ the IL [BuMelm]$^+$ [PF6] costs only 19.7 £ ml$^{-1}$. 
7 Zn removal and recovery for enhanced power output in three-chamber Microbial Fuel Cell

MFC performance and their potential to be implemented at large scale may be enhanced by utilizing the internal capacitance effect or applying control and optimization strategies as has been previously discussed. However, the integration or combination of MFCs with other processes and systems such as desalination, forward osmosis or capacitive desalination can extent the field of bioelectrochemical systems (BES) and their applications. Furthermore, the integration of RED with MFCs can even increase the cell potential. However to date, none of the integration approaches considers supported liquid membrane technology (SLM), a reactive extraction technique for metal removal.

This chapter deals with the integration of supported liquid membrane technology (SLM) with a Microbial Fuel Cell. The aim of the study was to develop and investigate the performance of a Bioelectrochemical system capable of removing metal ions from a metal rich wastewater, while producing electricity from the degradation of organic matter in a separate of concurrent wastewater stream. In a proof of concept study, an acetate-fed MFC was combined with an extraction technique for the separation of Zn\(^{2+}\) from an aqueous solution. The integration was carried out in the way that the cathode chamber contained the zinc wastewater and represented the feed phase for SLM separation at the same time. This configuration should increase the power production and simultaneously facilitate the removal of metal ions from the common cathode/feed chamber.

![Figure 7-1: Photo of MFC/SLM combination experiment.](image)
This approach enables the concurrent treatment of watercourses containing zinc ions and organic matter by converting the chemical energy content into electricity. Furthermore the process is suitable for the removal or recovery of several other candidate metals.

7.1 Results

This study aims to show the feasibility of a novel integration of MFC with liquid-liquid extraction (MFC/SLM). The results presented will focus on the performance improvement of the MFC in terms of the potential and power, as well as organic (acetate) and inorganic ($\text{Zn}^{2+}$) contaminant removal efficiencies. A key element of the study focused on the common cathode/feed chamber and the changes therein during operation, as well as the adjacent membranes forming containment on two sides, i.e. the bipolar and the supported liquid membrane, respectively (see Figure 7-1).

7.1.1 Separation of anode and cathode/feed chamber

Preliminary investigations were conducted into the efficacy of using an anion exchange membrane (AEM), CEM and combined AEM and CEM to provide appropriate ion transfer capabilities at the interface between the anodic chamber and the cathodic/feed chamber. The use of AEM resulted in the precipitation of zinc as an insoluble white phosphate salt in the combined cathode/feed chamber and was therefore found to be unsuitable for the presented application, as the aim is the removal in a form which enables electrolytic recycling. The use of a cation exchange membrane allows the transfer of $\text{Zn}^{2+}$ ions into the anode chamber which can harm the anodic biofilm, as $\text{Zn}^{2+}$ ions and particularly their complexes with anions such as $\text{Cl}^-$, have been found to be toxic to bacteria. The concentration at which zinc adversely affect bacteria will vary with the bacteria strain (H. Babich, 1978). Furthermore the transfer of $\text{Zn}^{2+}$ ions into the anode chamber will lower the recovery efficiency in the strip chamber. As a consequence a bipolar membrane was used between anode and cathode chamber to avoid any ion transfer apart from proton and hydroxide from the bipolar interface.
7.1.2 Development of cell potential

To test the system performance, the integrated approach (MFC/SLM) was compared to triplicate two chamber sub-system controls; namely the MFC sub-system and the SLM sub-system. Hence in total three different set-ups were tested.

Figure 7-2: Potential development in the MFC/SLM combination (black) and the MFC controls in gray (triplicate).

Figure 7-2 compares the potential development of the two chamber MFC control filled with 400 mg l\(^{-1}\) Zn\(^{2+}\) in the cathode chamber, to the 3 chamber MFC/SLM combination reactors. The MFC/SLM experiments were started by filling the cathode chamber and strip chamber simultaneously in order to avoid pressure differences on the membrane which might have led to membrane leakage. It can be seen that the voltage in the MFC/SLM combination increased immediately after starting the experiment. The performance on day 2 (24-48 h) was considered to be quasi steady state and the voltage was averaged over these 24 h (\(U_{ss}\)). The difference between the MFC control and the MFC/SLM was found to be 165 mV, with \(U_{ss}=472\pm5\) mV for MFC/SLM and \(U_{ss}=307\pm5\) mV in the MFC control. As the voltage was 53.9% higher, the substrate (10 mM acetate) was depleted more rapidly in the MFC/SLM combination experiment, so that the experiment was stopped after 72 h. The fluctuations which can be observed in all reactors at the same time, are as a result of mixing the cathode chamber before sampling and measuring the pH and conductivity.
Power curves were measured in two replicates of the MFC control and the MFC/SLM combination reactors. A maximum power point of 0.099±0.002 mW was achieved for the MFC control compared to 0.254±0.058 mW for the MFC/SLM combination. This represents an increase of 2.57 times over the control, and is ascribed to the lower internal resistance of the cell. The internal resistance where the maximum power point occurred was found to be 495±112 Ω for the MFC SLM experiment and 1072±216 Ω in the MFC control reactors. Hence the MFC control was operated close to the external resistance of R=1000 Ω.

Table 7-1: Performance parameters of MFC/SLM and MFC control averaged over t=24-48 h.

<table>
<thead>
<tr>
<th></th>
<th>MFC/SLM</th>
<th>MFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP (V)</td>
<td>722 ± 54</td>
<td>774 ± 18.4</td>
</tr>
<tr>
<td>voltage $U_{ss}$ (V)</td>
<td>472 ± 5</td>
<td>307 ± 5</td>
</tr>
<tr>
<td>current $i_{ss}$ (mA)</td>
<td>0.472 ± 0.009</td>
<td>0.307 ± 0.005</td>
</tr>
<tr>
<td>power $p_{ss}$ (mW)</td>
<td>0.223 ± 0.008</td>
<td>0.094 ± 0.000</td>
</tr>
<tr>
<td>energy (d 1-2) (Ws)</td>
<td>19.22 ± 0.71</td>
<td>8.129 ± 0.717</td>
</tr>
<tr>
<td>charge (d 1-2) (C)</td>
<td>104.6 ± 7.1</td>
<td>77.5 ± 2.0</td>
</tr>
</tbody>
</table>
Table 7-1 shows the key parameters determined during quasi steady state. The higher voltage in the MFC/SLM reactors compared to the MFC control resulted in a significantly higher average power of 0.223 mW in the MFC/SLM against 0.094 mW in the MFC control. The energy delivered during the second day was 137% higher in the integrated approach (19.22±0.71 Ws MFC/SLM; 8.13±0.72 Ws MFC).

7.1.3 pH development

The pH in the cathode or cathode/feed chamber was measured for all three different reactor configurations; the MFC/SLM reactors as well as their controls. As mentioned in section 3.8.5 the SLM control consisted of the feed chamber and the strip chamber separated by the liquid membrane. The cathode chamber also functioned as the feedphase for the MFC/SLM experiment and the SLM control and was filled with 400 mg l⁻¹ Zn²⁺ solution.

The pH dropped in all three reactor types immediately after the experiment was started. Also in the MFC control the pH was found to be pH=3 after 72 h. This indicates that more protons were transferred from the bipolar membrane than consumed by the ORR. In theory the pH should be constant as each electron produced through substrate oxidation should release one H⁺ to the cathode to maintain charge balance. This pH-drop was only observed
6. Catalyst and binder materials for oxygen reduction reaction

during the first 4 hours and from t=20 h onwards, the pH value remains constant at pH=3. The same was observed for the MFC/SLM and the SLM control, not least because of the logarithmic nature of the pH. However, the final values were significantly lower with pH=2.19 for MFC/SLM and pH=1.93 for the MFC control. This indicates that the proton concentration was not limiting the performance of the MFC. Furthermore it has to be kept in mind that the proton concentration correlates with the zinc removal, as every extracted zinc ion releases two protons into the cathode/feed chamber. Hence the pH value correlates with the zinc removal and seems to be higher in the SLM control. However, in the combined MFC/SLM systems some of these “extra” protons may be consumed by the oxygen reduction reaction.

7.1.4 Conductivity changes

pH value and conductivity of the anolyte were also measured at the beginning and the end of the experiment.

Table 7-2: Changes of pH-value and conductivity in the anode chamber.

<table>
<thead>
<tr>
<th></th>
<th>MFC/SLM</th>
<th>MFC control</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH(_{\text{start}}) (\text{-})</td>
<td>6.98</td>
<td>6.98</td>
</tr>
<tr>
<td>(\chi)(_{\text{start}}) (mS cm(^{-1}))</td>
<td>6.89</td>
<td>6.89</td>
</tr>
<tr>
<td>pH(_{\text{end}}) (\text{-})</td>
<td>6.81</td>
<td>6.85</td>
</tr>
<tr>
<td>(\chi)(_{\text{end}}) (mS cm(^{-1}))</td>
<td>6.66</td>
<td>6.77</td>
</tr>
</tbody>
</table>

In Table 7-2 it can be seen that the pH and conductivity in the anode chamber underwent small changes. Both parameters dropped slightly, which indicates that the buffer capacity of the 50 mM PBS was sufficient to keep the pH close to the optimum neutral pH. Again here the same principal as for the cathode chamber is valid for the anode chamber, hence theoretically for every electron and proton produced via oxidation, a hydroxyl ion should be released from the bipolar membrane through the anion exchange membrane facing the anolyte. Based on the results, it can be assumed that more hydroxyl ions were released in the first few hours, which is in accordance with the situation observed in the cathode chamber. The observed decrease in conductivity is a consequence of the acetate consumption.
6. Catalyst and binder materials for oxygen reduction reaction

Figure 7-5 shows changes in the conductivity (a) and proton concentration (b) in the cathode/feed chamber of MFC/SLM combination, MFC control and SLM control.

Figure 7-5 (a) shows a clear difference in the extent to which the conductivity increases with time. Only small conductivity changes were observed in MFC control and after 72 h the conductivity increased from 0.94 mS cm\(^{-1}\) to 1.35±0.03 mS cm\(^{-1}\). The conductivity in the MFC/SLM reactors increased to 2.870±0.170 mS cm\(^{-1}\), which was 1.083 mS cm\(^{-1}\) lower than the SLM control. Figure 7-5 (b) shows a strong correlation between the conductivity and the proton concentration over time. Hence the difference of more than 1.52 mS cm\(^{-1}\) between the MFC and MFC/SLM reactor is mainly a consequence of the higher proton concentration, which resulted in a difference of 5.46 mmol H\(^+\) l\(^{-1}\). Furthermore the conductivity losses, due
to the decreasing zinc concentration in the cathode chamber have to be taken into account (MFC/SLM and the SLM control experiments).

### 7.1.5 Removal of zinc ions and the recovery efficiency

The zinc concentration in the cathode/feed chamber and its accumulation in the strip chamber were observed during the experiment (see Figure 7-6). As can be seen almost all the zinc ions were removed from the cathode/feed chamber, so that after 72 h only 26±16 mg l$^{-1}$ remained in the MFC/SLM integrated reactors compared to 16±5 mg l$^{-1}$ in the SLM control. Consequently the Zn$^{2+}$ removal rate was not significantly influenced by integrating the MFC with SLM and the difference of 2.5% is far lower compared to the difference in the proton concentration (see Figure 7-5 (b)) and the expectations arouse from that observation. The proton concentration is expected to correlate with the zinc removal rate as two protons are transferred from the strip into the cathode/feed chamber for every Zn$^{2+}$ removed from the middle chamber.

![Figure 7-6](image_url)

Figure 7-6: Zinc removal and recover from the cathode/feed chamber in the MFC/SLM combination MFC and SLM control reactors.
It can be seen, that the MFC control, which just consists of anode and cathode chamber separated by a bipolar membrane, also removed some of the zinc. Within 72 h the zinc concentration decreased from 400 mg l\(^{-1}\) Zn\(^{2+}\) down to 200 mg l\(^{-1}\) Zn\(^{2+}\) indicating that some of the zinc was transferred through the cation exchange membrane into the transition area of the bipolar membrane. To exclude the existence of any transfer into the anode chamber where it could harm the biofilm, the zinc concentration was also measured in the anode chamber for all experiments. The zinc concentration was found to be below 26 µg l\(^{-1}\) in all reactors which derives in any case from the zinc in the mineral solution, which was added to the anolyte. Hence the zinc ions removed are accumulated in the transition area of the bipolar membrane.

The difference between the zinc removed and zinc re-extracted is 210 mg l\(^{-1}\) and 157 mg l\(^{-1}\) for the MFC/SLM combination and the SLM control respectively. This amount of zinc is stored as a complex with the carrier D\(_2\)EHPA in the pores of the supported liquid membrane and could be reduced by reducing the membrane thickness or decreasing the carrier concentration. The complexed zinc can be recovered if brought into contact with the strip solution (solvent extraction).

Also, the accumulation of the zinc ions in the strip chamber with the passage of time is presented in Figure 7-6. 39±6% of the zinc ions (157±23 mg l\(^{-1}\)) were recovered with the MFC/SLM approach compared 56±8% (227±32 mg l\(^{-1}\)) with the SLM control. The lower recovery in the MFC/SLM combination may be due to partial zinc transfer into the bipolar membrane, as monitored in the MFC control. Although with a lower proportion than in the MFC control as indicated by the amount of re-extracted zinc in Figure 7-6.

### 7.1.6 Coulombic efficiency and substrate removal efficiency

Table 7-3 presents the Coulombic efficiency and reduction efficiency of acetate in each of the triplicates as well as their averaged results.

515±5 mg l\(^{-1}\) and 439±63 mg l\(^{-1}\) of the acetate fed (530 mg l\(^{-1}\)) was depleted in the MFC/SLM and MFC control reactors respectively, during 72 h of operation. The lower acetate removal efficiency in the MFC control (82±11% vs 96±4%) is as a result of the higher voltage and the associated faster substrate depletion. As expected, the differences in the Coulombic Efficiencies were found to be low as the biofilm and the bacterial community should not be
affected by the MFC/SLM integration approach. As the bipolar membrane is relatively thick, it is more likely to be methanogenesis rather than oxygen intrusion which lowered the CE.

Table 7-3: Coulombic Efficiency and Reduction Efficiency of MFC/SLM and MFC control experiments in each of the reactor as well as the average values.

<table>
<thead>
<tr>
<th></th>
<th>Acetate reduction efficiency (%)</th>
<th>Coulombic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td></td>
</tr>
<tr>
<td>MFC/SLM 1</td>
<td>100</td>
<td>58</td>
</tr>
<tr>
<td>MFC/SLM 2</td>
<td>97</td>
<td>64</td>
</tr>
<tr>
<td>MFC/SLM 3</td>
<td>92</td>
<td>64</td>
</tr>
<tr>
<td>MFC 1</td>
<td>93</td>
<td>50</td>
</tr>
<tr>
<td>MFC 2</td>
<td>71</td>
<td>64</td>
</tr>
<tr>
<td>MFC 3</td>
<td>82</td>
<td>50</td>
</tr>
</tbody>
</table>

7.1.7 Bipolar and supported liquid membrane characterization

The changes in the resistance of both membranes with time were obtained by impedance spectroscopy. It can be seen that both membranes show an almost linear increase in their conductivities over 40 hours, although the rates differ.

Figure 7-7: Conductivity changes of supported liquid membrane and bipolar membrane measured in the MFC/SLM reactor.
The increase is more pronounced for the supported liquid membrane as can be seen in Figure 7-7. The SLM conductivity increased from 0.02 up to 0.16 mS cm\(^{-1}\) within 37 h whereas the bipolar membrane increased from 0.03 to 0.06 mS cm\(^{-1}\). The transfer of zinc into the transition area of the bipolar membrane, observed in the MFC control did not adversely affect the conductivity of the bipolar membrane.

To further investigate the ion transfer behavior from and into the cathode feed chamber, the concentration of different anions (nitrite, nitrate, fluoride, chloride, phosphate and sulphate) were measured by ion chromatography, in order to exclude such ion transfer.

![Normalized sulphate concentration in the cathode/feed chamber.](image)

Apart from sulphate (because zinc was present as ZnSO\(_4\)) only chloride (< 20 mg l\(^{-1}\)) and phosphate (< 30 mg l\(^{-1}\)) were found in the cathode feed chamber. Figure 7-8 shows the changes in the sulphate concentration normalized to the starting solution (SO\(_4^{2-}\)=569 mg l\(^{-1}\)), which was higher than the expected 400 g l\(^{-1}\). During operation, the sulphate concentration did undergo small changes; a decrease of less than 3% was found in the MFC and SLM control experiments and the MFC/SLM integrated approach resulted in an 8% increase.
6. Catalyst and binder materials for oxygen reduction reaction

Figure 7-9: Membrane permeability and diffusion coefficient of zinc through the supported liquid membrane.

The membrane permeability of the supported liquid membrane and the diffusion coefficient were determined for zinc (see Figure 7-9). The averaged Zn removal was fitted to a 1st order kinetic function. The membrane permeability of the MFC/SLM was determined to be $6.77 \times 10^{-7}$ and was $8.58 \times 10^{-7}$ m$^2$s$^{-1}$ for the SLM. Also the diffusion coefficients were in the same order of magnitude, with the SLM resulting in 20% higher values.

7.2 Discussion

7.2.1 Performance improvement

The results presented in this chapter show, that the integration of microbial fuel cell with supported liquid membrane technology is not only possible but also results in a significant voltage increase of $165 \pm 7$ mV compared to the MFC control. It was shown, that a common cathode and feed chamber resulted in a significantly higher pH and conductivity; both of these parameters lower the internal resistance of the cell. As protons are involved in the oxygen reduction reaction ($O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$, $E^0=1.23$ V) the potential will depend on the pH. Many air-cathode systems have a membrane or separator directly attached to the cathode and operate close to pH=7 and due to the limited proton availability high pH close to the cathode are observed, which adversely affect the cathode potential. The pH in the cathode/feed chamber of the MFC and MFC/SLM was found to be lower, hence the process
was not limited by the proton availability. The lower pH observed in the cathode/feed chamber lowered the activation losses of the ORR and increased the cathode potential. The increase in the cell potential originating from the lower activation losses, was calculated using the Nernst equation. The theoretical effect of the changing proton concentration on the cathode potential was $E = E^0 - \frac{RT}{zF} \ln \left( \frac{1}{[O_2][H^+]} \right)$, assuming a partial pressure for oxygen of 0.2 atm and is presented in Figure 7-10 (a). The anodic potential changes due to the decreasing substrate concentration were also considered ($E_{anode} = E^0 - \frac{RT}{8F} \ln \left( \frac{[CH_3COO^-]}{[HCO_3^-][H^+]} \right)$), assuming a bicarbonate concentration of 0.005M.

![Figure 7-10](image-url)

Figure 7-10: Changes in the anode and cathode potential of MFC and MFC/SLM according to Nernst equation (a), theoretical maximum cell potential difference (b).
Assuming linear acetate degradation over time, the changes in the anodic potential observed are not significant, as can be seen in Figure 7-10. The combined effect was always found to be below 59 mV (see Figure 7-10 (b)), which shows that other effects contributed to a greater extent to the achieved increase in potential.

Apart from the lower activation losses the higher proton availability was also shown to increase the conductivity significantly. This is also reflected in the internal resistance of the cell measured after 24 h. The internal resistance in the MFC/SLM (R=495 Ω) was half that of the MFC resistance (R=1072 Ω), which almost matched the external load resistance (R=1000 Ω). Hence optimization of the external load or controlling the external load with control strategies such as maximum power point tracking (Boghani et al., 2013b) could further enhance the performance of an integrated system. The ohmic potential losses of the combined system were also reduced by the increase of the bipolar membrane conductivity over time as observed in Figure 7-7.

The low pH in the cathode/feed chamber was also necessary to avoid the precipitation of the zinc as hydroxide which will start above pH=7.5, with the precipitation optimum at pH=9.2. Regarding the removal of other target metal ions, a low cathode pH is preferred, as many metals can precipitate under basic condition. Zhang et al. (2012d) for instance observed the formation of a copper hydroxide in an MFC cathode under basic conditions (pH=8.83). Hence this system, where a bipolar membrane maintains charge balance and the cathode chamber also receives additional protons from the supported liquid membrane does not cope with high pH values next to the cathode, as is common in other MFC systems and combination approaches, such as MDC and RED-MFC.

The difference in the acetate removal efficiency is due to the higher potential in the MFC/SLM reactor compared to the MFC and the Coulombic efficiency was found to be similar in two and three chamber reactors. Hence it can be concluded, that there is no effect on the CE during short term operation. A greater operational difference can be expected if a higher current is driven for longer than the 72 h period investigated.

7.2.2 Supported liquid membrane

The supported liquid membrane was impregnated with Di-ethylhexylphosphor acid as a carrier for zinc. This transfer mechanism is based on facilitated coupled counter transfer;
hence every carrier-zinc ion complex will release two protons into the cathode chamber which affects the pH in the common cathode/feed chamber.

The pH in the integrated MFC/SLM increased immediately (see Figure 7-4), as at the start the concentration of free carrier on the catholyte/supported liquid membrane interface is high. In general the formation of the complex and hence the reaction rate is fast and the diffusion of the zinc ions through the boundary layer on the catholyte/SLM interface limits the formation of the complex. The extraction rate is limited by diffusion of the $\text{Zn}^{2+}$/D$_2$EHPA complex through the liquid membrane. It is driven by the concentration gradient in the membrane, which is a result of the distribution coefficients of $\text{Zn}^{2+}$ at both aqueous/supported liquid membrane interfaces.

Both parameters, the proton and zinc concentration, influence the partition coefficient and therefore the removal rate of zinc ions. The membrane permeability and the diffusion coefficient for zinc through the LM were of the same order of magnitude ($P=10^{-7}$ m $s^{-1}$, $D=10^{-10}$ m$^2$ s$^{-1}$). Apart from the driving concentration gradient, the membrane permeability and diffusion coefficient can also be influenced by temperature and the viscosity of organic mixture.

The liquid membrane removed 93% of the zinc, which was comparable to the SLM control (96%). In theory the SLM technology can also benefit from integration with an MFC. As some protons will be consumed by the ORR, the pH value will not drop as fast as in the SLM reactor, which is beneficial for the partition coefficient on the catholyte/SLM interface as can be seen in Figure 2-8. The pH gradient is the main driving force and required to maintain the zinc transfer through the LM.

The small changes in the sulphate concentration in the cathode/feed chamber might have occurred by osmosis. Hence due to the higher concentration of dissolved particles in the strip chamber, water molecules might have diffused through the LM towards the strip chamber, to compensate the difference in dissolved charged particles. This could explain the small increase in $[\text{SO}_4^{2-}]$ concentration observed in the cathode/feed chamber. Furthermore $\text{SO}_4^{2-}$-ions might have been transferred through the LM. In general, the liquid membrane is immiscible with water; however, a small percentage might be adsorbed which can also influence the viscosity of liquid membrane. This might be the reason for the increase in the liquid membrane conductivity observed in Figure 7-7. As a decrease in the
viscosity of the extractant/organic solvent-mixture can have a positive impact on the Zn$^{2+}$ diffusion coefficient.

7.2.3 Bipolar membrane

In Figure 7-4 it was shown that the pH also decreased in the MFCs control cathode chamber. In theory the pH should be constant without splitting more water than necessary to maintain charge balance. Previous studies have either observed an increase in the proton concentration (Ter Heijne et al., 2006a) or the opposite phenomenon (Ter Heijne et al., 2007a). Bipolar membranes have to overcome a membrane polarization for the water splitting reaction to occur. This membrane polarization resistance was found to be lower at low current densities as produced in microbial fuel cells (Harnisch et al., 2008). This is a result of a so called leakage current, which accomplishes charge balance by ion transfer rather than water dissociation.

This leakage current was observed in the MFC control, where Zn$^{2+}$ was transferred to the interface of the bipolar membrane. However, there was still an excess release of protons observed in the MFC controls as the pH dropped to 3. The protons could also be released to compensate for the zinc transfer into the bipolar membrane. However, the difference of $0.99$ mM H$^+$ observed in the MFC control could explain a zinc removal of $32$ mg l$^{-1}$ but not a removal of $200$ mg Zn$^{2+}$ l$^{-1}$. Furthermore the polarization resistance is positively affected by low solution pH. Due to the low current densities and the low pH, the membrane polarization might be below the $0.830$ V suggested by the membrane manufacturer.

In general it was shown that the performance increase in the integrated system was mainly related to the pH, which reduced the activation losses at the cathode, increased the solution conductivity and so enhances the cell potential.

7.3 Conclusion

For the first time a Microbial Fuel Cell was integrated with Supported liquid membrane technology, which enhanced the power of the MFC subsystem by a factor of 2.4 times, due to a synergistic effects. If this power density at the proof of concept scale in this study is replicable, it represents an important outcome. Not only was the system performance increased, but the applicability of BES also extended. The combined MFC/SLM system
enables the simultaneous treatment of organic matter and removal of zinc ions from two parallel streams. The voltage was increased by 165±7 mV compared to the MFC control and 93% of zinc was removed within 72h. The higher voltage is mainly a consequence of pH related effects which had a positive impact on the activation and ohmic losses. Furthermore, the field of application can be extended as SLM technology can be used to selectively remove and accumulate other heavy metal ions by varying the extractant and/or controlling the pH in the aqueous phases.
8 Continuous zinc removal in three chamber MFC

8.1 Introduction

Having successfully integrated the two technologies of microbial fuel cells and supported liquid membrane extraction and operated the process in batch mode (Chapter 7), further experiments were carried out incorporating a continuously operated cathode/feed chamber. Hence an artificial zinc containing wastewater (100 mg l\(^{-1}\)) was pumped through the middle chamber and/or cathode chamber in the MFC controls.

A concentration of 100 mg Zn\(^{2+}\) l\(^{-1}\) was chosen, as this region of concentration is of special importance. Other techniques, such as precipitation are not practical at low concentrations and furthermore do not take recycling into account. Concentrations above 5 mg l\(^{-1}\) Zn\(^{2+}\) are already above the drinking water limit of the World Health Organization and can harm the bacteria as explained in section 2.8. Hence it is important to find an economical method to treat these low contaminated waste streams.

![Figure 8-1: Schematic illustration of the experimental set up of three chamber MFC/SLM and two chamber MFC control reactors for continuous zinc removal.](image)

40 g l\(^{-1}\) H\(_2\)SO\(_4\) and 210 g l\(^{-1}\) H\(_2\)SO\(_4\) were used in the strip chamber to drive the zinc removal from the cathode/feed chamber. Zn\(^{2+}\) removal is governed by the difference in pH between strip and feed phase and because every Zn\(^{2+}\) ion is replaced by two protons, this will ultimately affect the MFC/SLM performance due to the lower internal resistance and the lower cathodic activation losses, as the findings of the previous chapter have shown. Hence this chapter investigates the effect of different strip acid concentrations on the performance. Furthermore different membrane thicknesses were investigated to observe differences in the zinc removal rate, which might also affect the cell potential. Finally, some
pre-experiments on the electrolysis of zinc from the strip phase were carried out to determine optimum acid and zinc concentration, as the ultimate aim is not only the removal, but also the recycling of zinc.

8.2 Results

In the following section the affect of different sulphuric acid concentrations in the strip phase on pertinent parameters in the common cathode/feed chamber are presented. The effect of such concentrations on the internal resistance were investigated as well as the impact on the conductivity of the membranes. Two membrane thicknesses were tested to observe the difference in zinc transfer. The results presented herein represent the outcome of a parametric study which should help to define the optimum operating strategy and point to limitations as well as delivering ideas for further procedure.

8.2.1 Development of voltage in continuous mode

Figure 8-2: Voltage development of MFC/SLM with different strip acid concentrations (40 g l⁻¹ or 210 g l⁻¹ H₂SO₄) compared to the control (duplicates).

Figure 8-2 shows the potential of MFC control and MFC/SLM reactors at 40 g l⁻¹ or 210 g l⁻¹ H₂SO₄ measured over the duration of the experiment. It was shown that the MFC control
Reactors presented a significantly lower voltage ($U_{ss} = 201 \pm 5$ mV) compared to the three chamber reactors. The performance between day 2 and day 4 was relatively stable ($U_{ss}$) and the voltage was averaged over this period to compare the reactor types. During this period of time no significant potential difference were observed in the MFC/SLM reactors with different strip-acid concentrations. The average voltage was $575 \pm 5$ mV for $40 \text{ g l}^{-1} \text{H}_2\text{SO}_4$ and $592 \pm 7$ mV for $210 \text{ g l}^{-1} \text{H}_2\text{SO}_4$, as can be seen in Figure 8-3. However, the difference between the MFC control and the MFC/SLM reactors was more than $375$ mV and was therefore also significantly higher than the $165$ mV difference observed in batch mode (see Figure 7-2). Hence, the cell potential of the MFC/SLM benefits even more from the combination of the two technologies in continuous operation than in batch. The steady state power increased by more than 8 times (40 µW MFC compared to 331 µW and 350 µW in the MFC/SLM reactors over the control; see Table 8-1). After 6 days different characteristics were observed for the cell potential with different strip acid concentrations. During this period the cell potential was kept higher and as a consequence the substrate in the anode chamber was degraded sooner, when $210 \text{ g l}^{-1} \text{H}_2\text{SO}_4$ were used in the strip phase.

![Figure 8-3: Voltage development of MFC/SLM with different strip acid concentrations (210 g l$^{-1}$ H$_2$SO$_4$ (membrane thickness = 0.6 mm and 300 g l$^{-1}$ H$_2$SO$_4$) compared to the control. The experiments were carried out 6 months after the results presented in the figure above.](image-url)
Figure 8-3 presents the results obtained from the same reactors six months after the results presented in Figure 8-2 were obtained. The 210 g l⁻¹ H₂SO₄ MFC/SLM experiment was repeated to determine the repeatability and stability of the biofilm. In addition to the MFC control reactors, the figure contains the results obtained with a thicker SLM membrane (2 mm vs. 0.6 mm used in all other experiments) and with 300 g l⁻¹ sulphuric stripping acid. Similar results to those in the previous experiment (see Figure 8-2) were observed, but the steady state cell potential from the 210 g l⁻¹ H₂SO₄ MFC/SLM reactor was 70 mV lower than previously, as can be seen in Table 8-1. Also, the thicker membrane in combination with a higher strip acid concentration does not affect the cell potential significantly and gives comparable results to the 210 g l⁻¹ H₂SO₄ MFC/SLM experiment (membrane thickness = 0.6mm). The observed difference in potential between the 3 chamber integration and 2 chamber MFC reactors is again more than 300 mV in favour of the former, which represents a 6 fold higher power.

<table>
<thead>
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<th></th>
<th>V_avg (mV)</th>
<th>i_avg (mA)</th>
<th>p_avg (mW)</th>
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</thead>
<tbody>
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<td>MFC control</td>
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<td>0.201</td>
<td>0.040</td>
</tr>
<tr>
<td>40 g/l MFC/SLM</td>
<td>575 ± 5</td>
<td>0.575</td>
<td>0.331</td>
</tr>
<tr>
<td>210 g/l MFC/SLM</td>
<td>592 ± 7</td>
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<td>0.350</td>
</tr>
</tbody>
</table>

Results after 6 months

<table>
<thead>
<tr>
<th></th>
<th>V_avg (mV)</th>
<th>i_avg (mA)</th>
<th>p_avg (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2_MFC control</td>
<td>215 ± 25</td>
<td>0.215</td>
<td>0.046</td>
</tr>
<tr>
<td>2_210 g/l MFC/SLM</td>
<td>522 ± 6</td>
<td>0.522</td>
<td>0.272</td>
</tr>
<tr>
<td>2_300 g/l MFC/SLM</td>
<td>538 ± 8</td>
<td>0.538</td>
<td>0.289</td>
</tr>
</tbody>
</table>

Power curves were measured during steady state, by applying a constant potential to the anode and measuring the current response after stabilization, as can be seen in Figure 8-4.

The maximum power points (MPP) of the MFC/SLM reactors were 7.8-9 times higher than the control, which is again increased over that observed in batch mode (2.57). The internal
resistance determined from the power curves was $R=1313$ Ω in the two chamber control but was always below $R = 440$ Ω in the MFC/SLM control.

![Figure 8-4: Maximum power point characteristic of the two chamber and three chamber reactors with different strip sulphuric acid concentration.](image)

8.2.2 The impact of different strip acid concentrations on the cathode/feed chamber

Even though the cell potential did not vary significantly during steady state operation with different strip acid concentrations, a difference was observed in the pH/proton concentration and conductivity.

The starting pH of the 100 mg l$^{-1}$ zinc solution was 5. It can be seen that in continuous mode a similar behaviour to that in batch mode was observed as the pH initially drops in all reactor types. The cathode chamber pH of the MFC control drops immediately and remains almost constant around pH=3.7, which is higher than in batch mode (pH=3). This is a consequence of the middle chamber content ($V = 50$ ml), which is constantly being replaced at a flow rate of 70 ml d$^{-1}$.

The pH of the 210 g l$^{-1}$ and 40 g l$^{-1}$ H$_2$SO$_4$ MFC/SLM reactors differ, hence the strip acid concentration subsequently affects the conditions in the cathode/feed chamber (see Figure
8. Continuous Zn removal in three chamber MFC

8-5 and Figure 8-6). However, even though the pH of the middle chamber was lower in the 210 g l\(^{-1}\) MFC/SLM reactors, this difference had no impact on the cell potential during steady state.

![Figure 8-5: pH value in the continuously operated cathode/feed chamber by using different acid concentrations (duplicates).](image)

In both combination reactors (40 g l\(^{-1}\) or 210 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM) the pH value recovers after the initial drop and approaches the MFC control value towards the end of the experiment. Only the difference in cathode/feed chamber after the steady state (substrate depletion region) seems to have an influence on the cell potential (as indicated by the rectangle in the figure 8-5). This figure also contains the values for the thicker membrane and strip acid concentration of 300 g l\(^{-1}\). The effect of a thicker membrane can be observed over the first four days, were fewer protons reach the cathode/feed chamber even though the acid concentration is higher than in the 210 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM reactors. On the fifth day (\(t = 120\) h) a similar middle chamber pH was observed to that in the 210 g l\(^{-1}\) MFC/SLM reactor.

The conductivity in the cathode/feed chamber and the proton concentration calculated from the pH are presented in Figure 8-6. The conductivity changes in the continuous experiments appear to correlate with the proton concentration. A clear maximum in the conductivity can be seen in the MFC/SLM reactors. The 40 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM reactor
reached its maximum after 112 h ($\chi_{\text{max}}=8.51 \text{ mS cm}^{-1}$), whereas the 210 g l$^{-1}$ H$_2$SO$_4$ MFC/SLM reactors reached its maximum conductivity of $\chi_{\text{max}}=115 \text{ mS cm}^{-1}$ after a shorter period of time ($t=64$ h). The conductivity in the MFC control reactors stayed below 0.4 mS cm$^{-1}$.

Figure 8-6: Conductivity (a) and proton concentration (b) in the cathode/feed chamber during continuous operation (duplicates).
The proton concentration gradient between anode and cathode determines the diffusion of zinc through the LM and therefore also the counter transfer of ions. Therefore a SLM system consisting of the cathode/feed chamber and a strip chamber, undergoes constant changes in zinc and proton concentrations; it is only under steady state, when the distribution coefficients on the feed/membrane and membrane/strip interfaces are the same, that zinc transfer stops. The distribution coefficient is a function of the pH as well as the zinc concentration (see Figure 2-8). Changing the pH by one unit changes the distribution coefficient by a factor of 100. Figure 8-7 shows the pH after each of the experiments was stopped. It can be seen that the steady state phase described, was reached in both experiments after they were stopped. This is because the pH in the strip and cathode/feed chambers are too similar. As mentioned above the pH of the 40 g l\(^{-1}\) \(\text{H}_2\text{SO}_4\) experiment approached a similar pH to the MFC control. However, the strip acid pH was also in the same range even though the starting pH was below pH=1. The same phenomenon was observed for the 210 g l\(^{-1}\) \(\text{H}_2\text{SO}_4\) MFC/SLM reactor. In this case the equilibrium pH value in both chambers was lower (pH≈2.3), than with 210 g l\(^{-1}\) \(\text{H}_2\text{SO}_4\) (pH≈3.2). The anode chamber pH was measured at the start of the experiment (pH=7.12) and after the experiment finished (pH=6.9-7.5), hence no significant changes were observed.
8.2.3 Coulombic efficiency and COD removal efficiency

The Coulombic efficiency and the COD removal efficiency are shown in Figure 8-8. Due to the more rapid voltage drop in the 210 g l⁻¹ H₂SO₄ MFC/SLM reactor, the 40 g l⁻¹ H₂SO₄ reactor was operated for two days longer as well as the MFC control reactors (328 h), as the substrate depletion occurred earlier as can be seen in Figure 8-2. High COD removal efficiencies of more than 90% were achieved in the MFC/SLM reactors, as it was operated until the cell potential dropped to zero. As can be expected, the MFC controls achieved lower removal efficiencies due to the lower cell potential over the duration of the experiment. The Coulombic efficiency was found to be higher in the 40 g l⁻¹ H₂SO₄ MFC/SLM (CE=72%) than in the 210 g l⁻¹ H₂SO₄ and the MFC control (CE=47-48%).

8.2.4 Measurement of membrane impedance

Changes in the membrane conductivity were observed for both of the membranes used, as was considered in batch mode. The bipolar membrane had a higher membrane resistance than the SLM. Similarly to the observation made in batch mode, the membrane conductivity in continuous mode increased in the first three days, where it reaches its maximum. The maximum conductivity of the bipolar membrane is 54±2 μS cm⁻¹ and the SLM reached 112±10 μS cm⁻¹ on day three. It is noticeable, that the membrane
conductivities correlate with the conductivity measured in the cathode/feed chamber. This suggests that the solution conductivity influenced the membrane conductivity of both adjacent chambers.

![Figure 8-9: Bipolar membrane and supported liquid membrane conductivity changes in a 40 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM combination reactor.](image)

### 8.2.5 Changes in zinc concentration

As explained in section 3.8.7, the zinc concentrations could not be determined in all reactor replicates. In Figure 8-10 the zinc accumulation in the strip chamber was determined for the 210 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM (membrane thickness = 0.6 mm) as well as for the 300 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM and a thicker membrane (membrane thickness = 2mm). It can be seen that the zinc concentration in the strip chamber is linearly increasing during the first four days until the concentration saturates at around 80 mg l\(^{-1}\). The system behaviour in respect of zinc accumulation behaviour when using the thicker membrane differed from that using the thinner membrane and was lower for the first two days. This was as a result of the longer diffusion path for the complex through the membrane. Hence after 16 h, 45 mg l\(^{-1}\) were re-extracted in the 210 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM reactor, but only 12 mg l\(^{-1}\) in the 300 g l\(^{-1}\) H\(_2\)SO\(_4\) MFC/SLM reactor with the thicker membrane. After three days the same amount of zinc
was accumulated in the strip chamber of the 300 g l⁻¹ H₂SO₄ MFC/SLM reactor as in the 210 g l⁻¹ H₂SO₄ MFC/SLM reactor (c\(Zn^{2+}\),strip ≈ 75 mg l⁻¹).

8.3 Electrolytic zinc deposition the MFC/SLM reactor

Zinc was electrolytically recovered in the “strip chamber”, using an aluminium electrode as a cathode and a Pt wire as the anode; to determine the optimum conditions for a high current yield. Different zinc concentrations (10 g Zn²⁺ l⁻¹ and 70 g Zn²⁺ l⁻¹) and sulphuric acid concentrations (40 g l⁻¹ and 200 g l⁻¹ H₂SO₄) were tested to imitate the conditions in industrial processes, as presented in Table 2-2. Ultimately zinc should be accumulated to a
8. Continuous Zn removal in three chamber MFC

ccentration which makes the electrolysis economical, and suppresses hydrogen formation on the cathode. The highest average power was achieved with low zinc- and high sulphuric acid concentrations because of the lower internal resistance. However, this combination led to a relatively low current yield, as can be seen in Figure 8-11. The best combination of the highest power and current yield, was achieved with the highest acid and zinc concentrations (70 g l⁻¹ Zn²⁺ and 200 g l⁻¹ H₂SO₄), caused by the lower reactor resistance and reduced mass transfer limitations.

![Figure 8-11: Average power (a) and current yield (b) during Zinc electrolysis with different Zn²⁺ starting concentrations and different sulphuric acid concentrations, (c) Zinc deposition on Al electrode.](image)

It should be kept in mind that the pH in the electrolysis chamber will continually decrease due to water oxidation on the anode. Which represents a great method to decrease the pH, as would be required to maintain the zinc extraction and re-extraction with respect to the results presented above.
8.4 Discussion

8.4.1 Performance of the MFC sub-system

It was shown that compared to the experiments in batch mode, the performance in terms of cell potential and power production was even higher in the continuously operated cathode/feed chamber. This was found to be caused by the difference in internal resistance of the cell, in turn due to the higher catholyte conductivity and the lower activation losses at the cathode. The maximum power point was found to be 7.8-9 times higher in the MFC/SLM reactors than in the MFC control and the “pseudo steady state” cell potential was 375 mV higher than in the control reactors. When the experiment was repeated after 6 months, a slightly lower cell potential was observed ($\Delta U_{ss}$=72 mV). This is most likely due to community changes in the anode as a consequence to their exposure to light during this period of time. The formation of red bacteria in the anode chamber was observed after six months. These bacteria are likely to be a purple nonsulfur-photosynthetic bacterium, as reported by Xing et al. (2009). Their study reported that community changes were observed due to the presence of light, which led to the enrichment of photosynthetic microorganism; the exposure to light had a positive impact and increased the power density as reported for many photosynthetic fuel cells. Zhang et al. (2014a) observed the formation of light-induced red substances at low temperatures, which were found to be Arcobacter and Pseudomonas. In our case it was shown that the dominance of bacteria other than electrogens led to a significantly faster substrate depletion (see Figure 8-3) and therefore lower CEs. Hence in future experiments it is important to exclude light from the anode chamber.

8.4.2 Parameters related to pH and conductivity

The phenomenon of increasing cathode/feed chamber pH observed in batch mode was also observed in the MFC control. Hence a bipolar membrane releases more protons through the cation exchange membrane than charge balance requires, towards the cathode/feed chamber. The effect was less pronounced due to the continuous operation of the middle chamber. In general it was shown that a higher conductivity and lower pH did not affect the cell potential during steady state, as shown in Figure 8-2 and 8-3. The activation energy for the ORR is lowered by 59 mV per pH unit, but the difference between 40 g l$^{-1}$ and 210 g l$^{-1}$
H$_2$SO$_4$ MFC/SLM reactors was found to be less than 20 mV, even though a difference in pH of more than 1.47 was observed on day 3, which is in accordance with the theory.

The significant difference in the cathode/feed pH between the 40 g l$^{-1}$ and 210 g l$^{-1}$ H$_2$SO$_4$ experiments had no effect on the MFC and MFC/SLM reactor performance within the first six days, but seems to influence the voltage in MFC/SLM combination after day six considering the voltage drop behavior as discussed above. Changes in cell potential were observed from day six onwards, indicating that the proton concentration in the 40 g l$^{-1}$ experiment might become limiting, as a slow voltage decrease was observed from this point. The sharp decrease observed in the 210 g l$^{-1}$ H$_2$SO$_4$ combination indicates substrate depletion (acetate mass transfer limitations). Hence as indicated in Figure 8-5, a pH of 1.9 might be a threshold value for proton limitations for the presented system.

8.4.3 Membrane conductivities

It was shown that the bipolar- and supported liquid membrane conductivity correlate with the cathode/feed phase conductivity. The conductivity of the bipolar membrane was higher when the cell potential was also higher and more electrons were generated, resulting in a higher ionic current in the bipolar membrane (charge balance). In summary, it can be said that MFC sub-system performance depends on the performance of the SLM sub-system and the amount of protons being transferred from the strip to the common cathode/feed chamber. The supported liquid membrane conductivity depends on the driving force, which gradually decreases, as reflected in the membrane conductivity (see Figure 8-9). Hence the SLM conductivity correlates with the amount of H$^+/Zn^{2+}$ being transferred, to the point it reaches steady state and governs therefore the internal resistance and cell potential of the MFC-subsystem.

8.4.4 Performance of the SLM-sub-system

It was shown that the driving force (pH) between cathode/feed and strip chamber decreases during the time of operation until it reaches the equilibrium state where no zinc removal can be achieved. This is also reflected in the supported liquid membrane conductivity. Furthermore it has to be taken into account that sulphuric acid dissociates in two steps, hence in general sulphuric acid itself should also be able to maintain the pH
value to a certain extent. A proton removed due to the counter current transfer can be “regenerated” by dissociation due to the two protolyse steps of sulphuric acid:

\[
\begin{align*}
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} &\leftrightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+ \quad \text{pKa}_1 = -3 \quad (I) \\
\text{HSO}_4^- + \text{H}_3\text{O}^+ &\leftrightarrow \text{SO}_4^{2-} + \text{H}_3\text{O}^+ \quad \text{pKa}_2 = 1.92 \quad (II)
\end{align*}
\]

It was shown in practise that a higher sulphuric strip acid concentration cannot maintain zinc removal for longer, but results in a faster exchange mechanism and therefore a faster diffusion of Zn\(^{2+}\) and protons in counter current (see conductivity). As explained in section 2.9, the process is limited by diffusion; and diffusion is, apart from the temperature and its related parameters such as viscosity, a function of the concentration gradient. Hence the diffusion coefficient will change throughout the operation, according to the partition coefficient changes. To keep the zinc removal up for longer the pH values would have to be maintained ideally in both, but at least in one of the aqueous phases.

### 8.4.5 Zinc removal from the middle chamber

The zinc removal results indicate that in SLM, steady state phase was reached before the experiments were stopped, as the difference in the pH between the strip and cathode/feed chamber was too small to drive the process. Changes in the strip phase were not accessible, due to the reactor configuration and chamber volumes; therefore only the final pH values were determined, which were found to be similar in both aqueous phases.

Also, the zinc extraction presented in Figure 8-10 (b) indicates that the steady state of the SLM sub-system was reached before the cell potential dropped to zero and protons were transferred. Consequently the pH needs to be maintained, but the volume in the strip phase should not be increased (due to the addition of acids), as the process aims to re-concentrate the target ion and recycle it in a further step. The planned integration of hydrometallurgical zinc recovery directly in the strip phase offers the opportunity to create the protons resulting from water oxidation that are needed to maintain the driving force.

### 8.4.6 Comparison between batch and continuous mode

By comparing the results from the continuous mode with the results obtained in batch mode, it is noticeable that the continuous operation was beneficial for several performance
related parameters. A comparison of the “pseudo-steady state” parameters resulted in a significant increase in the cell potential of MFC/SLM combination reactors in continuous mode compared to the batch mode (165 mV batch; >375 mV in continuous mode).

The power increase from the MFC/SLM reactors compared to the MFC control reactors during steady state were significantly higher (8 fold increase) than in batch mode (2.3 fold increase). This is due to the higher cell potential of the MFC/SLM reactors in continuous mode and lower cell potentials of the MFC control reactors in batch mode. Even though 40 g l⁻¹ H₂SO₄ was also used as strip acid in batch mode, the cell potential under pseudo-steady state is more than 80 mV higher in continuous mode, as a result of the lower catholyte/feed pH. The difference in cell potential between the MFC control reactors in continuous and batch mode was 100 mV; also mainly due to lower catholyte pH in batch (pH≈3) compared to the continuous mode (pH≈3.7). As the catholyte gets replaced at a rate of 70 ml d⁻¹, which will wash out the excess protons released from the bipolar membrane. The resulting power curve was similar and by comparing Figure 7-3 and Figure 8-4 it can be seen that the maximum power point of the MFC control reactor in continuous mode are 50% lower, whereas the opposite was observed for the MFC/SLM reactors. The maximum power point increased and was found to be between 0.36 mW and 0.46 mW for the MFC/SLM reactors in continuous mode. In general it can be said that a continuous flow middle chamber is beneficial for the MFC/SLM integration, making it more promising for scaled up applications.

8.4.7 Outlook

![Diagram](image.png)

Figure 8-12: Different operation modes for MFC/SLM reactors for simultaneous electricity production and polishing.
The integration of MFC and SLM for simultaneous removal of heavy metal and organic waste offers several opportunities when it comes to reactor design or operation mode (Figure 8-2). Depending on the waste composition (metal and/or organic matter) the inorganic components could be removed first in the cathode/feed chamber before entering the anode chamber. As heavy metal ions are toxic, this could maintain a stable biofilm capable of producing electricity from the remaining organic matter. However, it is more likely that the MFC/SLM system could be fed with two different waste streams as presented in Figure 8-2. Waste streams from industrial processes, mining and waste ores can potentially be used in the cathode/feed chamber to recover zinc and furthermore other metal ions.

The performance of the integration approach presented, can be controlled by the surface area of the cathode (proton consuming) and the liquid membrane (proton delivering). Hence the pH in the common cathode/feed chamber could be controlled by the ratio of the surface area of liquid membrane and cathode. The surface area of the supported liquid membrane can govern the zinc removal velocity, together with the proton gradient. Advanced reactor design will have to consider all parameters and find a balance between the most important parameters (metal concentration, COD concentration, flow rate, membrane surface area and cathode surface area). Furthermore the pH in the strip phase could be controlled by the zinc electrolysis partially powered with the MFC. Hence the costs of the sulphuric acid for maintaining the proton gradient might be negligible as the electrolysis will produce two protons per deposited zinc.

### 8.5 Conclusion

The ultimate aim of the MFC/SLM integration reactor, apart from increasing the performance, is to remove and recycle zinc and/or other metal ions. As shown in the schematic illustration (Figure 8-13) zinc can be accumulated in the strip chamber and the electrolysis can be carried out directly from the strip chamber.

The set of experiments presented in this chapter, have shown that the MFC/SLM reactors can be operated with a continuous middle
chamber, showing an even higher power increase compared to the batch mode. Furthermore it was shown, that different strip acid concentrations will mainly affect the zinc removal rate and influence the power production less. A scaled up reactor type will need to be pH controlled to maintain zinc removal from the cathode chamber. One possibility is the addition of a strong acid. However, this could dilute the re-concentrated zinc solution. A better option will be to use the zinc electrolysis to maintain the pH as the oxidation of water releases protons while reducing zinc on the cathode.

The electrolysis can be partially powered using MFC power, or if several MFCs were connected in series, it is conceivable that the whole recovery can be powered by MFCs. Hence the whole process represents a low energy consuming technology for the treatment of several wastewater contaminants.
9 Discussion

The investigations carried out in the reported study give a broad picture of different ways to increase the applicability of MFCs and has investigated particular and plausible approaches. These different approaches were investigated to increase the applicability of MFCs by making their performance more competitive, through power increase, new integrations with synergistic processes and materials. The broader ambition was to bring the technology further towards industrial implementation through a scientific consideration of specific barriers. The experiments deal with the use of MFCs for industrial wastewater treatment and their effluent polishing efficiency, which represents the field of application where MFCs might mainly be used, as presented in chapter 4. The remaining studies deal with one specific bottleneck for MFCs, namely power quality, where the low cell potential and power dominate. Different approaches to overcome this issue have been considered.

There are several ways to increase the cell potential to a more useful level and the ones tested and presented in this thesis are associated with the internal capacitance which can be exploited in OC/CC operation (see chapter 5); enhancement of the catalytic ORR by selecting improved catalyst/binder systems as presented in chapter 6; or integration of MFCs with supported liquid membrane technology as presented in chapter 7 and 8.

Chapter 4 presents the results achieved with two different waste streams (effluent from a 2-stage bio-hydrogen/bio-methane process and separately, washdown water from a food producing company) treated in a tubular four module MFC. The aim of both studies was to investigate the COD removal potential and the effluent polishing capabilities of the systems. In the first study the energy recovery from the MFC as well as the whole anaerobic three stage process was determined. In total five different low organic loading rates were tested (OLR1=0.036 g sCOD l⁻¹ d⁻¹ to OLR5=0.572 g sCOD l⁻¹ d⁻¹) to determine the performance in terms of COD removal efficiency, CE and ECE. An organic loading of 0.572 g sCOD l⁻¹ d⁻¹ resulted in a power density of 3.1 W m⁻³ and the COD removal efficiency decreased from 35.2% (OLR1) to 4.41% (OLR5). The CE increased from 3.94-59.84%, but decreased significantly to 3.6% when the undiluted effluent (4.427 g sCOD l⁻¹ d⁻¹) was used. The pseudo-half saturation concentration for the 4-module tubular reactor fed on the BioH₂/BioCH₄ effluent resulted in \( K_s = 436.6 \text{ mg COD l}^{-1} \) (\( R = 1000 \Omega \)). The energy recovery varied from 0.33 J l⁻¹ (OLR1) to 92.95 J l⁻¹ (OLR5). The ECE was calculated on the basis of total COD concentration entered the tubular MFC as well as on the basis of the COD
reduction in the reactor. Both values are influenced by the CE and therefore increase from OLR1 to OLR5 (energy content for COD of 13.896 kJ kgCOD$^{-1}$ (Heidrich et al., 2010)). The ECE$_{\text{total COD}}$ increased from 0.05 to 0.81% and ECE$_{\Delta\text{COD}}$ from 0.14 to 18.24%. The energy recovery from the whole anaerobic three stage process increased marginally to the range of 71.36%, which comprised 0.24-0.40% from bio-hydrogen, 42.38-70.93% from bio-methane and 0.02-0.03% from bioelectricity production, on the basis of the above energy content for COD. However, the energy recovery of the MFC is only reported for a four module reactor and a higher recovery can be expected with an extended module count, as chemical energy remained available for further electrogensis.

Also another wastestream (washdown water from a food producing company) was tested in the same four module tubular MFC reactor in two different operation modes. The modes differed in terms of buffer concentration (PBS; 35 mM vs 3 times 50 mM), circuit control (100 $\Omega$ static load vs MPPT control) and operation (steady state vs continuous cycle). The starting organic loading rate was 2.79 g sCOD l$^{-1}$ d$^{-1}$. After 7 cycles 84% of the sCOD (960 mg l$^{-1}$) were removed in mode A and 70% (800 mg l$^{-1}$) in mode B, with respect to the effluent concentration. It was shown that mainly acetic acid was consumed first and propionic acid increased initially before depletion after 7 cycles, showing that higher carbohydrates were degraded during the effluent polishing process. It was shown that the MPPT control resulted in a faster proton release, which made the addition of buffer during the operation necessary.

Chapter 5 deals with the pseudo-capacitive behavior of a two modular tubular MFC with carbon veil anode and cation exchange membrane/air cathode as a mechanism to enhance power quality and energy efficiency. The pseudo-capacitance consists of a non-Faradaic component along with the charge storage capability of the carbon veil and electrogenic biofilm. Accumulated charge and energy with the anodic biofilm after prolonged open circuit times (1-120 min) were compared against equivalent periods of steady state loading (R=100-3000 $\Omega$). A significant difference in the amount of accumulated charge with different loads was observed, resulting in 1.051 C (R=100 $\Omega$) compared to 0.006 C (R=3 k$\Omega$).

An automated application of short open and closed circuit (0.5-10 s) cycles resulted in an increase of power/current production (if closed circuit alone is considered), but presented lower efficiencies considering the aggregated open and closed circuit periods. The cumulative charge on the carbon veil electrode with biofilm was 39,807 C m$^{-2}$ at R=100 $\Omega$. When different external loads were used (100-3 k$\Omega$) the lowest resistance resulted in the
9. Discussion

highest gain of 30-150 mV immediately after OC times of 1 to 120 min, whereas OC-periods of only 0.5-10 s resulted in voltage increases of 45-125 mV, showing that short OC/CC are beneficial when exploiting the capacitance effect.

EIS was used to investigate the anodic capacitance at different applied potentials (-0.5 V to +0.2 V vs Ag/AgCl), which showed that the Helmholtz layer presented a double layer capacitance of more than ten times higher than the double layer capacitance of the biofilm on the electrode. Aggregating both components (Helmholtz layer and biofilm double layer capacitance) resulted in a capacitance of 114-196 mF, depending on the applied potential.

**Chapter 6** deals with improvements on the cathode side of the MFC. Two types of ionic liquids, which are immiscible with water and exhibit ionic conductivity (one out of the two exhibits proton conductivity), were investigated as binder materials in combination with Pt and FePc as catalyst. Half cell studies were undertaken (CVs, LSV) revealing that ILs in combination with Pt resulted in higher current densities than with FePc as electrocatalyst; the current density peaks were higher than for the common binders Nafion and PTFE. Compared to the peak reduction current of the commercial 10% Pt electrode at -0.2 V vs Ag/AgCl, the prepared carbon paste electrodes revealed a reduction peak towards a more positive potential at 0 V vs Ag/AgCl.

A new integration approach was introduced in **chapter 7 and 8**, in which a MFC was integrated with supported liquid membrane technology for the treatment of waters containing organic matter and zinc ions. The 3 chamber reactors were first operated in batch mode in a proof of concept study, with 10 mM acetate in the anode (mixed cultured biofilm), 400 mg l⁻¹ Zn²⁺ in the common cathode/feed chamber and 40 g l⁻¹ H₂SO₄ in the strip chamber. The resulting MFC/SLM steady state voltage was 165 mV higher than the cell potential of the MFC control reactor. The power was 0.233 mW in the MFC/SLM compared to 0.094 mW in the control MFC. After three days of operation the pH in the middle chamber dropped to 2.1 in the MFC/SLM compared to pH=3 in the control, resulting in a conductivity difference of 1.08 mS cm⁻¹. The CE and the substrate removal efficiency of the MFC/SLM were found to be similar to the MFC control. The conductivity changes of the membranes during the operation were measured via EIS spectroscopy and within the 72 h the conductivity of the SLM increased more significantly than the bipolar membrane used to separate anode and cathode/feed chamber. The diffusion coefficient of Zn²⁺ through the liquid membrane in the MFC/SLM (4.26*10⁻¹⁰ m² s⁻¹) was 20% lower than in the SLM control (5.41*10⁻¹⁰ m² s⁻¹). The zinc removal from the cathode/feed chamber was 93±4% which is
similar to those obtained in the SLM control (96±1%), while the power output was significantly increased.

Previously in chapter 8 can be seen results from further investigations into the MFC/SLM system, operating it with a continuously fed middle chamber and different sulphuric acid concentrations (40 g l⁻¹ and 210 g l⁻¹) in the strip chamber. The results have shown that the enhanced power was also maintained and increased when operated in continuous mode for 14 days. The maximum power point obtained from polarization curve was 0.048 mW in the MFC control compared to 0.366-0.464 mW in the MFC/SLM reactors. No significant influence was found on the power output when different strip acid concentrations were used, even though a significantly lower pH value (and higher conductivity) was observed during the operation period. The maximum conductivity measured during the time of operation was 8.51 mS cm⁻¹ in the 40 g l⁻¹ MFC/SLM compared to 115 mS cm⁻¹ in the 210 g l⁻¹ MFC/SLM reactor. The equilibrium state of the zinc removal (similar pH value in strip and cathode/feed chamber) hence the point where the zinc transfer stops was found to occur at an earlier point in time when a higher strip concentration was used. The membrane conductivities were measured and found to be in accordance with the results from the batch mode (increase in the first three days and higher conductivity of the SLM compared to the bipolar membrane), but were found to decrease during the remaining 11 days.
10 Conclusion and further work

This chapter seeks to draw conclusion on the objectives introduced in section 1.1 and presented here again for convenience, and associated with the conclusions drawn.

Objectives:

To investigate the effluent polishing capability of a tubular MFC design processing a real wastewater under different operation strategies.

To investigate the integration of MFCs into a system with other anaerobic bioprocesses to increase the energy recovery.

The experiments revealed that a tubular reactor design is applicable for the treatment of real wastewater and for 2-stage AD effluent polishing. The real waste streams tested (2-stage AD effluent and chilled food manufacturing washdown water) exhibited a relatively high VFA concentration and conductivity. These two parameters were found to be essential/necessary for high power production in MFCs as a higher conductivity will lower the internal resistance of the cell. Due to the power limitations caused by the ohmic resistance, it might be worthwhile from an economical point of view to increase the conductivity by the addition of salts or preferentially buffer, but only if the power gain compensates for the additional costs, as the addition of buffer is not considered to be a sustainable strategy.

A pH drop was observed when the reactor was operated at its maximum power point (MPPT control). This pH drop can harm the electrogenic biofilm and limit the necessary proton transfer to the catalytic cathodic oxygen reduction reaction. To decrease the internal resistance and enhance the current to a useful level, a number of modules could be connected in parallel.

The performance in terms of power production, COD removal and CE was found to be dependent on the organic loading rate, but moreover on the amount of easily degradable substrate. In order to degrade higher carbohydrates present in more complex wastewater into VFAs, which will be consumed by electrogens along the reactor lengths, a multi-modular reactor will be required.

The CE of real waste streams was found to be significantly lower at higher organic loading rates (>0.6 g COD l⁻¹) and also the COD removal efficiency was found to decrease with
increasing organic loading. Hence the organic loading rate and consequently the CE will vary along the reactor length in a multi-modular reactor together with the ECE; hence more modules are required to increase the conversion efficiency. However, the efficiency might not increase significantly as the second stage effluent contains the entire recalcitrant load and furthermore it is likely that the AD effluent has to be sieved before entering the reactor to avoid clogging the reactor.

**Objective:**

*Identification of strategies to increase MFCs applicability by increasing the cell voltage and the concomitant power output from MFCs. More specifically, to investigate using capacitance and intermittency to increase voltage or by integration with other complementary systems to enhance the usability of the power produced.*

When the capacitance effect evident in a tubular two module MFC was tested in alternating open and closed circuit mode, it was found that duty cycling can increase the average cell potential, if averaged over the open circuit time only but results in lower overall energy efficiencies when compared to steady state operation under constant load (over the open and closed circuit time together); leading to the conclusion that an increase in voltage is only possible at the expense of energy efficiency.

A switched operating mode of period and timing to maximize the effect may be applicable where an array of multiple MFC reactors could be connected and integrated with an optimized electrical loading strategy. The scheduled switching strategy could produce power of suitable quality and consistency to be directly applicable to powering electronic devices such as sensors and microprocessors.

OC/CC duty cycling could be applied to benthic fuel cells, where methods such as serial connection fail to increase the voltage because of the interconnection of cells through the liquid phase. In this study the capacitance of the whole reactor was investigated under realistic conditions with the intention of increasing the power and current intermittently without the need of external power enhancing devices. Hence, periodic power harvesting could be used independently or in combination with other power management devices such as DC/DC converters to power small electronic devices and external capacitors, thus enhancing the applicability of MFC technology.

It was concluded that the capacitance is composed of a non-faradaic and a faradaic component, the latter resulting from the electrogenic electron transfer. The non-faradaic
component results from the double layer capacitance between the electrolyte/membrane/electrode interface on the cathode and the electrolyte/biofilm/electrode interface on the anode side, as the biofilm itself can contribute to the double layer capacitance due to charged components on the bacterial cell. The faradic component is thought to derive from the charge storage capability of bacteria in their outer cytochromes, charged during open circuit operation. Also, the electrons can be stored in the carbon veil anode during open circuit until the final open circuit potential is reached.

Objective:

To investigate electrode systems to enhance the catalytic oxygen reduction reaction. The significant challenge of PGM replacement, without comparative loss of performance, will be addressed from the point of view of empirical studies on catalyst/binder systems.

For the first time ionic liquid binder based, carbon paste cathodes were prepared for application in MFCs. The study, in which different binder catalyst systems for the catalytic ORR were tested in half cell measurements, revealed that the catalytic activity of the tested electrocatalysts platinum and iron(II)phthalocyanine, is dependent on the binder system and in the case of Pt it will also depend on the ionic liquid binder loading.

The results revealed that ILs can be used as binder material in carbon paste electrodes for ORR. The performance in terms of catalytic activity measured as current density in LSV half cell study revealed that the binder material has to be chosen with consideration to the electro-catalyst (Pt or FePc). Hence the catalytic activity of each catalyst was found to be dependent on the chosen binder material and in the case of Pt, activity was also a function of the IL-binder loading. However, further experiments need to be carried out to find the optimum catalyst loading.

Objective:

To investigate the benefits of integrating bioelectrochemical systems capable of removing heavy metal ions, with MFCs. The technology of liquid membrane permeation specifically should be integrated into a microbial fuel cell system in order to extend the applicability and explore possible synergistic effects.
The integration of MFC with supported liquid membrane technology for simultaneous removal of zinc and organic matter was carried out for the first time and was not only found to be possible but also resulted in a significant increase of power of 2.4 times. The synergistic effect was a result of several pH related effects which had a positive impact on the cell potential. The ORR potential was increased and lowered the activation losses, and the conductivity increased, which lowered the ohmic resistance of the cell.

The MFC/SLM integration offers many possibilities for the treatment of certain contaminants, as the selective removal and accumulation can be extended to other metal ions by varying the extractant and/or controlling the pH values in the aqueous phases. Furthermore it was shown that different strip acid concentration will mainly affect the zinc removal rate and less influence the power production.

The MFC/SLM system operation with continuous middle chamber (cathode/feed chamber) resulted in similar improvements in power, and was found to be possible also with low concentration of 100 mg Zn$^{2+}$ l$^{-1}$. The strip phase can therefore be operated in batch mode adjacent to the continuous without membrane leakage due to pressure differences. Hence zinc could be re-concentrated in the strip chamber until a certain concentration is reached at which point the electrolytic zinc recovery becomes economical. The electrolysis could be directly carried out from the strip chamber and could be partially powered using MFC power, or if several MFCs were connected in series, the whole recovery might be powered by MFCs.

In order to maintain the zinc removal from the cathode chamber and accumulation in the strip chamber a pH gradient has to exist between the two aqueous phases. One possibility is to deploy external pH control by the addition of acid, or if the electrolysis is carried out from the strip phase, the oxidation reaction of water will produce an equivalent amount of protons to the deposited zinc and can therefore simultaneously sustain the proton gradient. Therefore the integration represents a promising technology with low energy consumption as both systems synergistically support each other in terms of power enhancement and zinc removal and recycling.
10.1 Further work

Further experiments with real waste streams need to be done in a multi-modular tubular MFC (as presented in 3.8.1) to investigate the effluent polishing capability further. This will offer a deeper view into the degradation characteristics throughout the reactor including changes in the CE. Recording the pH value after a certain number of modules might reveal, if pH control is necessary in a scaled up 10 l reactor developed by Boghani (2014).

The results presented in chapter 6 show, that ILs are promising binder materials for MFC air-cathode systems, but have only been tested in half cell conditions to date. Hence the paste needs to be applied to carbon cloth, normally used in MFC systems, as it is more flexible than the brittle carbon paper electrodes, in order to investigate if a similar performance can be achieved with a different carbon base material. These electrodes should be tested in a cubic MFC by recording polarization curves and EIS spectra to study and compare the activation losses.

Ideally the FePc catalyst should be pyrolized to achieve a higher catalytic activity, which currently can’t be undertaken in our lab.

Once implemented in the cubic MFC, the long term performance should be investigated and observed in terms of cathodic biofouling. The paste composition could be further improved by testing different catalyst/carbon/binder ratios in half cell conditions, ideally on a rotating disc electrode to exclude mass transfer limitations.

The integrated MFC/SLM reactor offers many research directions. However, one of the most important future experiments will be the continuous zinc removal from the cathode/feed chamber and following electrolytic zinc recovery once a certain re-concentration has been reached. Additionally, the selectivity of the carrier used (D$_2$EHPA) towards other metal ions in the cathode/feed chamber has to be investigated.

The reactor design should be changed by placing the liquid membrane between the anode and cathode with either facing the strip chamber, or the feed chamber facing the air-cathode. This configuration will increase the cell impedance but is likely to have a positive impact on the extraction rate due to the additional driving electrochemical potential gradient.
11 References


11. References


11. References


References


11. References


11. References


11. References


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11. References


12 Appendix

ADDITIONAL RESULTS

Table 12-1: Composition of phosphate buffer with vitamins and minerals

<table>
<thead>
<tr>
<th>Contents</th>
<th>Concentration (g L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Buffer</strong></td>
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</tr>
<tr>
<td>NH(_4)Cl</td>
<td>0.31</td>
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<tr>
<td>NaH(_2)PO(_4)·H(_2)O</td>
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<td>Na(_2)HPO(_4)</td>
<td>4.33</td>
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<tr>
<td>KCl</td>
<td>0.13</td>
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<tr>
<td><strong>Vitamins</strong></td>
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<tr>
<td>Biotin</td>
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<tr>
<td>Folic acid</td>
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<td>Pyridoxine HCl</td>
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<td>Thiamin</td>
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<td>Pantothenic acid</td>
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<td>B-12</td>
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<td>4-aminobenzoic acid</td>
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<td>Lipoic acid</td>
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<td>Nitrilotriacetic acid</td>
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<td>MgSO(_4)·7H(_2)O</td>
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<td>MnSO(_4)·H(_2)O</td>
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<td>FeSO(_4)·7H(_2)O</td>
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<td>ZnCl(_2)</td>
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Table 12-2: Results impedance measurement on tubular reactor with varying module number in parallel connection (see section 4.1.3).

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<th>Mode C</th>
<th>Mode D</th>
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<td>$R_{ohm}$ (Ω)</td>
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<td>$R_{anode}$ (Ω)</td>
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<td>$R_{cathode}$ (Ω)</td>
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<td>2.65</td>
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<td>$C_{anode}$ (F)</td>
<td>6.25</td>
<td>3.78</td>
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<td>$C_{cathode}$ (F)</td>
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<td>0.023</td>
<td>0.030</td>
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<tr>
<td></td>
<td>0.52</td>
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Table 12-3: Control experiments for experiments on washdown water; the feed was filled in bottles and kept at room temperature (CRT) or at 4 °C-fridge (CF) – see section 4.1.3.

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<th>cycle</th>
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<th>pH</th>
<th>conductivity Χ (mS cm⁻¹)</th>
<th>Acetic acid (mg l⁻¹)</th>
<th>Propionic acid (mg l⁻¹)</th>
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**SCIENTIFIC OUTCOME**

**Papers**


**Conferences**


**Fradler, Katrin**; Kim, Jung Rae; Richard M. Dinsdale, R.M; Guwy, A. J.; Premier, G. C. ,(Sept. 2012) Investigation of the internal capacitance effect of a tubular Microbial Fuel Cell with air-cathode and high surface carbon veil anode, EU-International Society for Microbial Electrochemistry and Technology, ISMET conference, Ghent, Belgium poster presentation


