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**ANODE AND ELECTROLYTE SELECTION TO IMPROVE HYDROGEN RECOVERY
IN MICROBIAL ELECTROLYSIS CELLS**

A Thesis in
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by
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ABSTRACT

A microbial electrolysis cell (MEC) is a bioelectrochemical system that generates hydrogen from organic matter. A biofilm of microbes grows on an anode and oxidizes the organic matter, and then the electrons are transferred to a conductive cathode to electrochemically produce hydrogen gas. Conductivities of wastewaters vary, influencing the solution resistance, and therefore affecting the extent of treatment, current, and gas production. In order to scale up MECs, it will be necessary to reduce the spacing between the electrodes (to reduce the reactor width per pair of electrodes), but to still produce the same amount of hydrogen per projected area. Brush anodes have shown greater power densities than felt anodes in microbial fuel cells (MFCs), as brush anodes can be placed closer to the cathodes than felt anodes without power being adversely affected. However, oxygen crossover is not a factor for current generation in MECs. In this study, flat carbon felt anodes were compared to carbon brush anodes to determine if current densities and hydrogen production rates were affected by the type of anode. The use of flat anodes could reduce the width of the anode chamber, increasing the overall hydrogen production rate per volume of reactor for the same current. In addition, the impact of solution conductivity was examined to see if higher electrolyte conductivities could improve hydrogen production rates in MECs, as they do for current in MFCs.

MFCs with carbon brush in a 2 cm long chamber or carbon felt anodes in a 4 cm long chamber were batch fed with sodium acetate in a 50 mM phosphate buffer solution (PBS). Following acclimation to this medium, the MFCs with the felt anodes produced a maximum power density of $0.80 \pm 0.02 \text{ W/m}^2$, which was lower than that of the brush anodes ($1.69 \pm 0.10 \text{ W/m}^2$). These power densities were consistent with previous studies for both types of electrodes. The anodes were transferred and acclimated to two chamber MECs with anion exchange membranes and platinum carbon cathodes in the same medium until similar current was produced

for at least 3 cycles. The brush anode MECs had a higher hydrogen production rate of 0.38 ± 0.02 $\text{m}^3\text{H}_2/\text{m}^3\text{d}$, with an average current density (current for 90% of the total charge transferred, I_{90}) over the cycle of 4.2 ± 0.5 A/m^2 . The MECs with felt anodes had a lower hydrogen production rate of 0.32 ± 0.02 $\text{m}^3\text{H}_2/\text{m}^3\text{d}$ consistent with the lower current ($I_{90} = 3.4 \pm 0.1$ A/m^2). The extent of acetate removal for a cycle, based on the change in chemical oxygen demand (COD) was also greater for the brush anode MECs ($89 \pm 2\%$) than the felt anodes ($71 \pm 2\%$). The sharp decline in the current during a fed batch cycle of the MECs with the felt anodes suggested a diffusion limitation of substrate to the anodes, which could have reduced hydrogen production compared to brush anode MECs. To test this hypothesis, the anolytes of the felt MECs were stirred to improve mass transfer to the anode biofilm. Stirring increased the hydrogen production rate of the felt anode MECs by 8% to 0.41 ± 0.04 $\text{m}^3\text{H}_2/\text{m}^3\text{d}$. The I_{90} and COD removal also increased to 5.1 ± 0.4 A/m^2 and $92 \pm 1\%$. By improving mass transfer into the felt anode in an MEC with mixing, the current density, COD removal, and hydrogen production rate became comparable to that obtained with brush anode MECs.

When the solution conductivity was increased to 100 mM PBS in MFCs, the power density improved for the felt anodes (1.00 ± 0.04 W/m^2), but it was still lower than that produced using brush anodes (1.25 ± 0.12 W/m^2). The MFCs with brushes showed a decline in power compared to the 50 mM tests, likely as a result of the higher phosphate concentration or oxygen intrusion adversely affecting the microbial community. When the anodes from these reactors were transferred into MECs, the decreased solution resistance did not improve the hydrogen production rate or average current density for the MECs with brush (0.37 ± 0.10 $\text{m}^3\text{H}_2/\text{m}^3\text{d}$, 3.9 ± 1.6 A/m^2), but did for the felt anodes (0.40 ± 0.04 $\text{m}^3\text{H}_2/\text{m}^3\text{d}$, 3.7 ± 0.4 A/m^2). Increasing the solution conductivity reduces solution and membrane resistance, but only improved hydrogen production rates for the felt anode MECs.

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Chapter 1

Introduction

The Earth has seen an overall warming trend that is affecting the atmosphere, resulting in an increase in extreme weather events, ice melts, sea level rise, ocean acidification, and other changes [1]. Climate change is human driven, especially by greenhouse gases produced everyday [45]. Greenhouse gases include carbon dioxide, methane, nitrous oxide, and others that can trap heat inside the atmosphere [1]. Eighty percent of total carbon emissions due to humans is generated by energy production from coal, oil, and gas. To help reduce the amount of carbon released by humans, renewable energy sources can be used, including solar, wind, nuclear, and hydroelectric [23]. Another way to lower the effects of climate change is to find ways to reduce the amount of electricity used every day. Wastewater treatment plants alone use 3% of the total electricity produced in the US [51]. A typical wastewater treatment plant uses aerobic processes like an aeration basin and clarifier, but the cost of energy for these processes could be half of the entire wastewater treatment process [30]. Biological electrochemical systems (BES) are alternative treatment processes that can be used to reduce the net energy consumed by conventional wastewater treatment plants.

Hydrogen gas is carbon-free energy carrier that is used in many industrial processes, but currently most hydrogen gas is produced using fossil fuels [2]. From 2008 to 2014 refineries have increased hydrogen gas consumption by 60%, but production has decreased by 1%. For hydrogen gas to be a reliable energy carrier, and to reduce the amount fossil fuels used to currently produce it, alternative production methods are necessary [20]. Microbial electrolysis cells (MECs) are a type of BES being studied to both produce hydrogen gas and reduce the amount of energy used in wastewater treatment plants. MECs are an anaerobic process where

microorganisms transfer electrons to a conductive anode, which are then carried through a circuit to a cathode [30]. Using a catalyst, the electrons from the cathode combine with protons to produce hydrogen gas. The reaction is an endothermic process under standard conditions and at neutral pH, so when acetate or other similar organic substrates are used as fuels, additional voltage is needed [31]. The minimum applied voltage to initiate the microbial electrolysis process is $-\Delta G_r^\circ/nF$, where ΔG_r° is the Gibbs free energy of the reaction at standard conditions, n is the number of electrons involved in the reaction and F is Faraday's constant (96,485 C/mol e^-) plus any losses due to over potential and internal resistance in the system. While only 0.114 V is needed to produce hydrogen using acetate (assuming an anode potential of -0.3 V), in practice it has been found that at least 0.25 V of applied voltage is needed to produce hydrogen gas at appreciable rates [30].

There are many variables that can change the performance of MECs including the anode and cathode materials, pH, electrolyte conductivity, and electrode spacing [31]. To better compare the impacts of these variables on hydrogen production, the rates of hydrogen production are normalized by electrode areas and reactor volumes. If the volume of the reactor can be decreased while producing the same rate of hydrogen per area of electrodes, then this would increase the hydrogen production rate per volume of reactor. While felt anodes have been compared to brush anodes in Microbial Fuel Cells (MFCs) and showed a lower power density due to oxygen intrusion from the air cathode [3], the anodes have not been compared in MECs without the presence of oxygen. The large surface area of brush anodes allows a more extensive microbial growth on the electrodes, so the biofilm on the brush is typically not adversely affected by oxygen crossover from the cathode [33]. Without oxygen, it is unknown whether the large surface area of brush anodes would still be beneficial relative to flat anodes.

The internal resistance of an BES can be decreased in many ways to improve MFC or MEC performance [53]. The use of higher conductivity solutions in single-chamber MFCs [53]

and in the catholyte of MECs [53-54] have been shown to reduce ohmic resistance and increase performance. Two-chamber MECs have high internal resistance due to the need for the membrane to obtain pure hydrogen gas rather than methane [12,29], and therefore they generally have lower gas production rates than single-chamber MECs. However, the use of higher solution conductivities could reduce both ohmic and membrane resistances [15]. While the use of higher conductivities in the catholyte has been examined in previous MEC studies [41,54], the use of higher solution conductivities in both the catholyte and anolyte has not been tested.

The objective of this study was to determine if flat carbon felt anodes in MECs, without oxygen intrusion, have a hydrogen production rate comparable to the more commonly used carbon brush anodes. The same general reactor architecture was used for all reactors with 2 g/L sodium acetate as the fuel in 50 mM phosphate buffer solution (PBS). The MECs with the different anodes were compared on the basis of current densities, COD removals, hydrogen production rates, and energy recoveries. A second objective was to determine if higher solution conductivities could be used to improve hydrogen production rates for these systems, by increasing both the concentration of the PBS buffer in the anolyte and catholyte from 50 mM to 100 mM.

Chapter 2

Literature Review

While MECs have only been studied for a little over a decade, many improvements have been made in the cost of materials used in MECs and their performance. Materials and reactor configurations have been a large focus to determine the most economically feasible options at a larger scale, while also producing a high volume of hydrogen gas per volume of reactor. Various suitable wastewater and effluent options with different solution conductivities have been considered for large scale MEC implementation, so a high energy efficiency can be achieved and the maximum amount of hydrogen gas can be recovered. The literature important to operation of MECs and their development process with regards to electrode spacing, anode materials, and solution conductivity are reviewed below.

2.1 Exoelectrogens

Microorganisms that can biologically oxidize organic matter are needed to make bioelectrochemical systems possible [32]. The exoelectrogenic microbes release electrons from the oxidation of organic matter and transfer them to the anode. The electrons from the anode are then transferred to the cathode, producing current. BESs can be powered by simple compounds like acetate or more complex substrates like those in the organic matter in human and animal wastewaters. There are specific microorganisms that are known to have electrochemical capabilities like *Geobacter sulfurreducens*, which has been used to power MFCs [32]. In one study, a pure culture of *Geobacter sulfurreducens* PCA was compared to that of mixed cultures in identical MECs [7]. The mixed cultures produced higher hydrogen production rates, but based on 16S rRNA analysis, 72% of the bacterial community was *G. sulfurreducens*, suggesting a

majority of the microorganisms in this mixed culture were this specific exoelectrogenic bacterium. Acetate fed MECs inoculated with wastewater have a substantial amount of *G. sulfurreducens* in the anodic biofilm [7]. *G. sulfurreducens* have also been found to be within a diverse microbial community for a large scale MEC using winery wastewater as the feed that initially produced hydrogen gas [12]. While pure culture bacteria can be used in MECs, they are not practical for wastewater treatment application, and do not produce current densities much greater than MECs with mixed culture bacteria [7].

In lab scale BES, it is common to use acetate in a buffered solution, but the choice of buffer has been shown to have an effect on the microbial community [26]. Phosphate buffer and bicarbonate buffers are the most commonly used, but it was shown that if only bicarbonate was used in a MEC, the abundance of *Geobacter* in the microbial community was low. With a phosphate-rich buffer, *Geobacter* reached up to 60% of the microbial community. This study determined that for MECs, the phosphate/bicarbonate ratio should be about 20% [26]. However, some *Geobacter* species such as *Geobacter sulfurreducens* do not grow well in solutions with high phosphate concentrations or salinities [6].

Geobacter anodireducens are another species of *Geobacter* that has been found to have similar characteristics to *G. sulfurreducens* [46]. Part of the reason why these two strains are different is that *G. anodireducens* cannot reduce fumarate using acetate, unlike *G. sulfurreducens*. The benefit of growth of *G. anodireducens* is that this microbe can grow in media with 3% NaCl, while *G. sulfurreducens* can only tolerate about 1.5% NaCl. The ability for this species to tolerate a higher concentration of salt became especially apparent when they were cultivated in a BES [46].

2.2 Anode materials for MFCs

The anode is essential to the performance of different BESs because that is where the electroactive biofilm grows. The anode material needs to be conductive, non-corrosive, have a high porosity, and a high surface area for the microbes [30]. Carbon cloth, carbon paper, graphite felt, carbon brush, and more have all been tested in various types of BESs. Carbon fiber brushes are the most commonly used because they have a high surface area of fibers per volume, which can sustain the biofilm growth, they can have a relatively low cost, and they have been shown to produce higher power densities than other anode materials in MFCs [30].

A baseline set of conditions can help to determine what factors can impact MFC performance [49]. While many types of anodes and chemical treatments of anodes have been studied, one study examined different materials that were all used in 4 cm cubic chamber MFCs with a 50 mM PBS electrolyte, compared to brush anodes that were heat treated, with platinum carbon cathodes. A comparison of studies using felt anodes [3,57], carbon cloth [17,28], and brush anode studies [25,34,36,38-39,42,44,48,50,55,58-60], showed that brush anodes had the highest power densities [50]. Based on these different studies, the average maximum power densities were $1.11 \pm 0.45 \text{ W/m}^2$ for the brush anodes, $0.79 \pm 0.19 \text{ W/m}^2$ using felt anodes, and $0.51 \pm 0.00 \text{ W/m}^2$ with carbon cloth anodes. When the cathodes were varied in the carbon felt studies, the average power density increased to $1.30 \pm 0.27 \text{ W/m}^2$, which is higher than the brush average. Although a platinum carbon cathode was not used as a control in most of those studies, so it did not prove that the felt was comparable to the brush anodes [53].

Many types of anode treatments have been suggested to improve power generation in MFCs. If carbon felt is the focus due to the high porosity and large area available for bacteria growth [3], it can be determined if there is a treatment that would produce a comparable power density to that of brush anodes. Various thicknesses of carbon felt anodes only using heat

treatment were tested in MFCs to determine the effects on power production. When the felt thickness increased from 0.32 to 1.27 cm with a 4 cm electrode spacing, the power densities increased from 0.60 W/m² to 1.05 W/m², but these power densities were all lower than that produced using 2.5 cm long brushes with activated carbon cathodes (1.30 W/m²) [18]. The felt thickness did not improve performance when the electrodes were placed close together due to oxygen intrusion from the air cathode [3]. Another study with a continuous flow MFC with a platinum coated carbon cloth cathode and a wrapped carbon felt anode with 100 small holes to allow flow through the felt produced a maximum power density of 0.12 W/m² [13]. This small current density was due to the high cathode surface area (72 cm²) and high solution resistance (115 Ω). A study that had a carbon paper cathode (64 cm²) with a carbon felt anode treated the anodes using nitric acid activation by soaking or deposited a polyaniline polymer onto the surface using a layer technique after the nitric acid soaking [21]. The two treatments proved to have a 50% and 87% improvement on the maximum power density of 0.16 W/m² for untreated felt MFCs. Another treatment option was applying ruthenium oxide (RuO₂), using a 0.05 M ruthenium chloride solution, onto a carbon felt anode [35]. This treatment enhanced the maximum power density to 3.08 W/m², which was 17 times greater than a carbon felt anode treated with hydrogen peroxide. The improvement was indicated to be due to a lower anode resistance and higher specific surface area that allowed for more microbial growth. An activated carbon felt anode with a platinum carbon paper cathode was shown to improve power to 2.07 W/m², 58% greater than an untreated carbon felt anode [60]. The enhanced power could be due to the change in surface functional group, which supported a better bacteria adherence and growth. Based on these articles, MFC power densities with carbon felt anodes can be improved by surface treatment, but it was not clear in many of the studies if the treated felt anodes would have performed better than brush anodes as they were not directly compared in the same reactors.

Treatment of carbon fiber brush anodes has also been shown to improve MFC performance. By soaking the acid in pure acetone, ammonium peroxydisulfate, and sulfuric acid, and then heating the anode at 450°C for 30 minutes, power improved by 34% to 1.4 W/m² in MFC tests [14]. With only heat-treating the anode, the increase in power was 15% (1.3 W/m²). Although the acid improved the performance even more than the heat treatment, if complexity of the acid treatment and cost is taken into account, the ammonia gas treatment is not necessarily needed for better anode performance. This idea of cost and complexity can also be applied to the felt treated anodes due to the expensive chemicals being used for treatment. When MFCs are used at larger scales, it will be more difficult and more expensive to treat anodes, so it may not be practical to use complex or expensive processes to treat anodes even though performance could be improved.

2.3 Anode materials for MECs

The same types of anodes that have been used in MFCs can also be used in MECs, as the main function of the anodes is to provide a high surface area for exoelectrogenic microorganisms [24]. In MECs, however, oxygen crossover is not an issue. Thus the main focus on the performance of anodes in MECs is current density and hydrogen gas production. Like MFCs, different anodes, for example various thicknesses of felt anodes, have been tested in MECs. A larger MEC reactor (50 mL anode and cathode chambers) operated under continuous flow conditions was tested with carbon felt as the anode [16]. Various cathode and anode configurations were tested to determine the optimal set up. The purpose of this was to also test the thickness of the anode in an MEC. Like MFCs, it was found that the current density increased in MECs with felt thickness, but in MECs it was observed that hydrogen recovery did not increase with current density. When the number of cathodes was increased to produce a stacked electrode

design, the current density increased but instead of an increase in hydrogen gas, there was an increase in methane gas. Due to the spacing increase when more electrodes were added, it was concluded that it is possible to increase current, but to see an increase in hydrogen production the spacing between the anode and cathode should be minimized [16].

Carbon brush anodes are commonly used in MECs due to their high performance and low costs [12]. A two-chamber MEC with a total volume of 58 mL and an anion exchange membrane separating the chambers, produced a hydrogen production rate of $1.1 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$ and peak current of $3.4 \pm 0.5 \text{ mA}$ using 50 mM PBS and 1.5 g/L sodium acetate [42]. The anode was a 2.5 cm brush and the cathode was stainless steel mesh. This was a low hydrogen production rate compared to a single chamber MEC with a 2 cm electrode spacing using a brush anode ($17.8 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$) and 1.0 V applied voltage [11]. In a 1000 L pilot-scale single chamber MEC, six brush anodes were used for each anode-cathode module containing six stainless steel cathodes [12]. Soluble COD removal was $62 \pm 20\%$ and gas production was $0.19 \pm 0.04 \text{ L/L/day}$. The anode did not seem to limit current generation, but instead the reactor architecture and the inoculation procedure were critical to the performance.

MEC anodes can be inoculated and initially acclimated in MFCs, or directly acclimated in MECs. The impact of acclimation in MFCs versus acclimation in MECs, however, has not been well examined. In one study it was shown that current and hydrogen production did not vary significantly between anodes inoculated in MFCs and switched to MECs once stable conditions were reached, and anodes that were directly inoculated in MECs, for treatment of a fermentation effluent [47]. However, the coulombic efficiency was up to 7% higher for anodes inoculated in MFCs compared to anodes only acclimated in MECs. Acclimating anodes in MFCs before transferring them into MECs is the most commonly used method for lab scale experiments, but this procedure would not be practical for pilot scales due to the need for different reactor architecture and cathodes [12]. Therefore, when MECs are to be used at a larger scale, similar

anodes to those in MFCs can be utilized, but will most likely need to be inoculated directly in the MEC reactor.

2.4 Reactor Configuration

Electrode spacing has been studied to improve reactor performance. With a solution concentration of about 100 mM NaCl and a carbon paper anode, it was found that decreasing the distance between the anode and cathode from 4 cm to 2 cm in an MFC increased the power density, coulombic efficiency, and energy recovery [29]. When the electrode spacing was reduced from 2 to 1 cm for an MFC operated in fed batch mode, with a 50 mM phosphate buffer solution (PBS) as the electrolyte, the power density decreased due to the reduced performance of the bacteria on the anode [10]. With a 2 cm electrode spacing, and flow from the anode to the cathode chamber, there was a lack of dissolved oxygen transfer from the cathode to the anode, so the bacteria on the anode were not impacted by oxygen crossover and the power density improved with this reduced electrode spacing [10]. When reducing the spacing between the electrodes, oxygen transfer to the anode needs to be considered due to its adverse effects to the bacteria.

The impact of reduced electrode spacing in MFCs was also examined when various felt anode thicknesses were tested [3]. In one configuration, the felt anode and cathode were placed 4 cm apart. In the other set up, a separator electrode assembly (SEA) was used by placing the anode and cathode directly next to each other with a separator and supporter in between. While the SEA configuration reduced ohmic resistance due to the reduced electrode spacing, power was not improved, indicating that oxygen transfer through the cathode adversely impacted power generation. The conclusion was that thicker anodes improved performance due to more anode volume and more surface area for microbial growth, but reactor configuration was a factor due to oxygen crossover [3]. Felt anodes with reduced electrode spacing from the cathodes in MECs

have not been extensively studied in MECs. Without the oxygen used at the cathode, it is possible that the felt anode and cathode could be placed closer together to reduce ohmic resistance without adverse impacts due to oxygen transfer to the anode that occurs in MFCs.

Depending on the electrode configuration, hydrogen crossover could affect hydrogen gas recovery in MECs. Methane in MECs can either be produced by hydrogenotrophic methanogenesis from hydrogen crossover or by acetoclastic methanogenesis from acetate:



Production of methane is more common in MECs from hydrogenotrophic methanogenesis due to the gas produced at the cathode chamber crossing over to the anode [49]. Thus, hydrogen gas is lost to methane generation, decreasing the amount of hydrogen gas recovered. Single chamber MECs are more likely to yield a mixed biogas instead of pure hydrogen because of the presence of methane. Two chamber MECs have an ion exchange membrane between the electrodes, which reduces the amount of hydrogen that is transferred to the anode [9]. Although a much higher purity of hydrogen gas can be recovered in two chamber MECs, methane has consistently still been observed in the product gas [9]. It is possible that with a decrease in electrode spacing, the hydrogen could more easily be transported to the anode and produce methane, but this impact of electrode spacing relative to hydrogen gas crossover has not been studied.

2.5 Conductivity

While a reduced electrode spacing can be used to decrease internal resistance, increasing conductivity can also reduce solution resistance. The solution resistance (R , Ω) is proportional to the electrolyte conductivity by $R = l/(\sigma A)$ where l is distance between the electrodes (cm), σ is the electrolyte conductivity (S/cm), and A is the projected surface area of the electrodes (cm²) [5].

To avoid potential losses, ohmic resistance needs to be minimized. Ohmic resistance is due to ion transport through the solution, a membrane if present, and the resistance between the electrode and current collector [30]. If it is assumed that the resistance between the current collector and electrode is negligible, and there is no electrode overpotential, the ohmic resistance can be assumed to be the solution resistance. The ohmic resistance of an MFC can then be estimated by measuring the solution conductivity and electrode distance.

In single chamber MFCs it has been shown that with increasing conductivity, higher power and current densities can be achieved [33]. The higher conductivity reduces the ohmic resistance, which has been shown using electrochemical impedance spectroscopy (EIS). An increase of phosphate buffer concentration of 50 mM to 200 mM showed a decrease in ohmic resistance from 18.3 ohms to 6.8 ohms [53]. In single chamber MFCs, solution resistance is one of the biggest losses of voltage, so by using higher conductivity solutions, there can be a significant increase in performance. With 400 mM phosphate buffer, however, MFC performance did not improve even when the electrode spacing was reduced [29]. The lack of enhanced performance could be due to the high salt concentration, which can adversely impact microbial growth and current generation [29,37]. This demonstrates that there is a limit to how much the ohmic resistance can be improved by increasing conductivity in MFCs due to the adverse impact of higher salinities or phosphate concentrations on bacterial growth [7,29,37].

Single chamber MECs have the same limitations as MFCs in terms of salt concentration being a factor in the ohmic resistances and current generation by bacteria. While single chamber MECs have higher current densities they suffer from significant loss of hydrogen to methane production [12]. While two chamber MECs produce nearly pure hydrogen gas, the ohmic resistance is increased due to the use of a membrane. Ohmic resistance can still be reduced in two chamber MECs by reducing electrode spacing to minimize solution resistance, and increasing the solution conductivity. Increasing the catholyte conductivity from 50 mM phosphate buffer

solution to 100 mM or 200 mM has been shown to decrease the overall resistance within an MEC, improving the hydrogen production rate by 43% [54]. It has also been shown that adding sodium chloride to the catholyte improves hydrogen production rates better than increasing the phosphate buffer concentration. High solution conductivities in both the anolyte and catholyte chambers in MECs has not been studied, but from an electrochemical perspective, it should reduce ohmic resistance in both chambers and improve MEC performance.

Chapter 3

Comparison of hydrogen production with two types of anodes in two chamber microbial electrolysis cells with increased solution conductivity

Abstract

Flat anodes placed close to the cathode to reduce electrode spacing in microbial electrolysis cells (MECs) could improve current densities, as there is no oxygen crossover from the cathode to the anode that could reduce performance as observed in microbial fuel cells (MFCs). The use of flat carbon felt anodes placed close to the cathode was compared to larger graphite fiber brush anodes in fed-batch, two chamber, cubic type MECs using 50 mM or 100 mM PBS electrolytes. With 50 mM PBS, the brush anodes had a higher hydrogen production rate of $0.38 \pm 0.02 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$, compared to $0.32 \pm 0.02 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$ using felt anodes. The diffusion of the substrate was demonstrated to limit the performance of MECs with felt anodes by stirring the anolyte, which resulted in a hydrogen production rate ($0.41 \pm 0.04 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$) similar to that of the MECs with brush anodes. When the solution conductivity was increased to 100 mM PBS, the brush and felt anode MECs had similar performances to the 50 mM PBS reactors. The felt anode MECs had a similar hydrogen production rate ($0.40 \pm 0.04 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$), but lower current density ($3.7 \pm 0.4 \text{ A}/\text{m}^2$) than with the 50 mM stirred anolyte felt MEC reactors ($5.1 \pm 0.4 \text{ A}/\text{m}^2$). The highest hydrogen production rates were therefore obtained with brush anodes likely due to the immersion of the brush in the anolyte and its close placement to the cathode.

3.1 Introduction

Microbial electrolysis cells (MECs) are a promising renewable hydrogen production technology that can be used to avoid the need for fossil fuels as a source for hydrogen gas

production [2]. Fossil fuels have continued to drive the increase of the carbon dioxide concentration in the atmosphere leading to climate change. The consumption of hydrogen gas by refineries has increased by 60% from 2008 to 2014, but production from fossil fuels has decreased by 1% [20]. Hydrogen gas is an alternative energy source, since its product is water and not CO₂, but a more sustainable generation that does not use fossil fuels is needed.

MECs use wastewater or fermentation effluent as the fuel for exoelectrogenic biofilms on anodes to electrochemically produce hydrogen at a cathode [30]. MECs are completely anaerobic systems that can produce an electrical current and hydrogen gas, but they require the addition of voltage to the circuit to drive hydrogen gas production. Microbial fuel cells (MFCs) are another alternative energy source that use similar materials and architectures as MECs, except oxygen is used as the electron acceptor, and electricity is produced without the need for external power [30]. Multiple anode materials have been tested in both systems, but carbon brush anodes have been proven to be the best electrode material in MFCs [53]. A previous comparison of felt anodes with different thicknesses in MFCs [3] showed that for the thickest felt, power production ($1.05 \pm 0.03 \text{ W/m}^2$) was similar to an average maximum power density for brush anodes in MFCs ($1.11 \pm 0.45 \text{ W/m}^2$) [53]. However, close electrode spacing of the flat anode and cathode was limited due to the adverse impact of oxygen intrusion on the anode biofilm [3]. Felt anodes were also tested in a larger continuous flow MEC design (50 mL anode and cathode chambers) [16]. A multiple anode set up was analyzed, but while current increased with a thicker anode and a stacked electrode set up, hydrogen gas production did not improve. It was concluded that unlike MFCs, using felt anodes in MECs required minimized spacing between the anode and cathode [16]. However, with close electrode spacing in MECs, hydrogen crossover could become an issue even when using an ion exchange membrane. The hydrogen could use microorganisms on the anode to produce methane instead of the desired pure hydrogen [49]. The impact of reduced electrode

spacing with the lack of oxygen while using a flat anode needs to be tested in small fed-batch MECs to determine its influence on hydrogen production.

While the conductivities of electrolytes and wastewaters that have been used in bioelectrochemical systems can vary, the greater the solution conductivity the less solution resistance, and so based on just electrochemistry this should increase current [53]. Previously it has been shown that an increase in conductivity to about 200 mM PBS increases power in MFCs due to the decreased ohmic resistance [53], but if the conductivity is higher, salt concentrations can adversely impact performance [27, 37]. An increase in conductivity from 50 mM PBS to 100-200 mM PBS was tested in the catholyte of two chamber MECs [41, 54]. Like in MFCs, an increase in conductivity in the cathode chamber improved current densities and thus hydrogen production. It has not been examined whether an increase of conductivity in both the anode and cathode chambers of an MEC improves performance.

In this study, I compared the performance of flat felt anodes to the commonly used brush anodes in MECs. Previous tests have mainly used brush anodes, since it is known that these are conductive, inexpensive, and have high surface areas. While felt anodes did not perform as well in MFCs due to oxygen intrusion and continuous flow MECs because of a larger electrode spacing, they have not been tested in small batch mode MECs with reduced electrode spacing. An increase in solution conductivity has been tested in MFCs and the catholyte of MECs, but has not been tested in the anode and cathode chambers of MECs. In this study the brush and felt anodes were tested with a solution conductivity of 50 mM PBS and 100 mM PBS, and the performance was compared by measuring the hydrogen production rate, COD removal, and energy recoveries.

3.2 Materials and Methods

3.2.1 MFC reactor configuration

Single chamber MFCs were used to acclimate and test the power of MFCs using different anodes (Fig. 3-1a). Two anode materials, a high cylindrical surface area anode (brush) and a high porosity flat anode (felt), were compared in the MFCs (Fig. 3-1b). Brush anodes (2.5 cm length, 1.5 cm diameter) were made from carbon fibers and twisted between titanium wire (PANEX 33 160K, ZOLTEK) and placed in the middle of the 2 cm reactor with a volume of about 14 mL [31]. Carbon felt anodes (0.64 cm thick) were cut into circles with a 7 cm² cross sectional surface area. To minimize the impact of oxygen intrusion on the flat anode, felt anodes were placed on the opposite side of the chamber from the cathode, in a 4 cm long cube reactor with a volume of about 28 mL instead of the 2 cm long chambers [3]. All anodes were heat treated for 30 min at 450°C in a muffle furnace before being placed in the MFCs [31]. The cathode for the reactors were activated carbon cathodes produced by VITO (Mo, Belgium) [55].

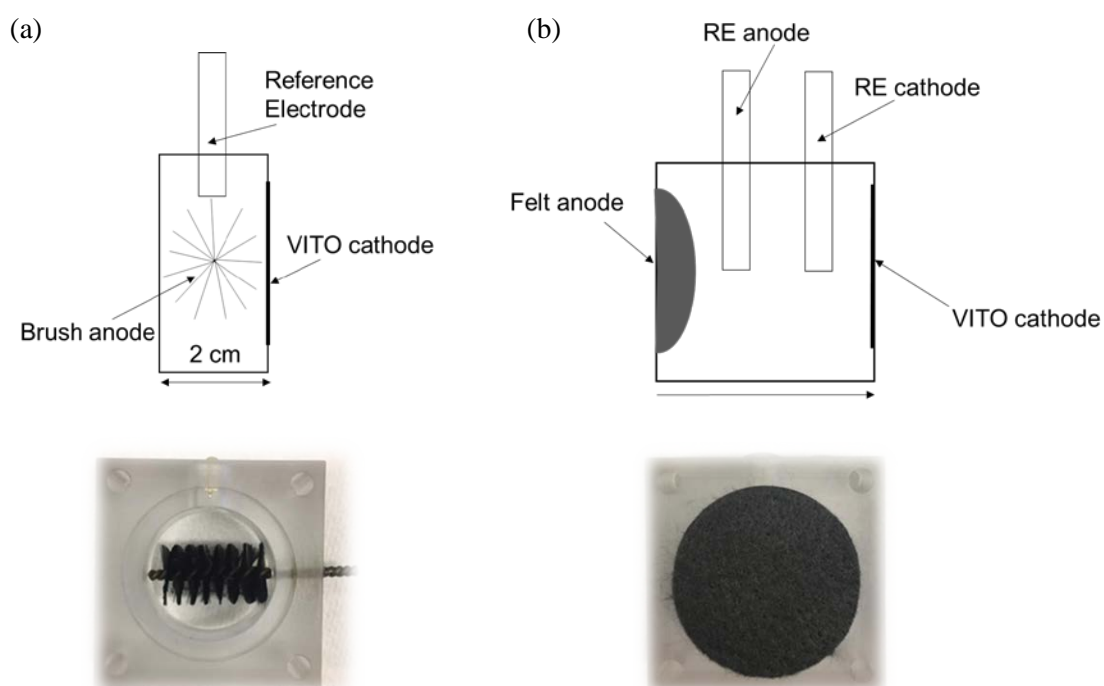


Figure 3-1: MFC configuration and anode placement for (a) brush and (b) felt.

3.2.2 MEC reactor configuration

Two chamber MECs were constructed from 2 cm long anode chambers and 4 cm long cathode chambers, both with 3 cm diameter cylindrical chambers constructed with polycarbonate (Fig. 3-2) [8]. The anode and cathode chambers were separated by an anion exchange membrane (AEM, Selemion AMV, AGC Engineering Co. Ltd., JP) with an anode chamber volume of ~14 mL and cathode chamber of ~35 mL. Headspace gas was collected using a tube attached at the top of the cathode chamber, with the tube sealed with a butyl rubber stopper and aluminum crimp cap [41]. The gas was collected using a needle through the stopper, and a tube connected to a 100 mL gas collection bag (Cali-5-Bond, Calibrated Instruments, NY). The anode chambers for the brush anodes were the same 2 cm reactor operated in MFCs. The felt anodes, taken out of the MFCs, were placed in a 2 cm reactor against the AEM and a circular titanium foil current collector. The cathodes for all reactors were 7 cm² stainless steel mesh circles with a platinum and carbon mixture (ETEK C1-10, 10% Pt and Vulcan XC-72) using a Nafion binder (5 wt% solution, Aldrich Nafion® perfluorinated ion-exchange resin) as previously described [41]. They were suspended 1 cm away from the AEM within the cathode chamber with the catalyst facing the membrane.

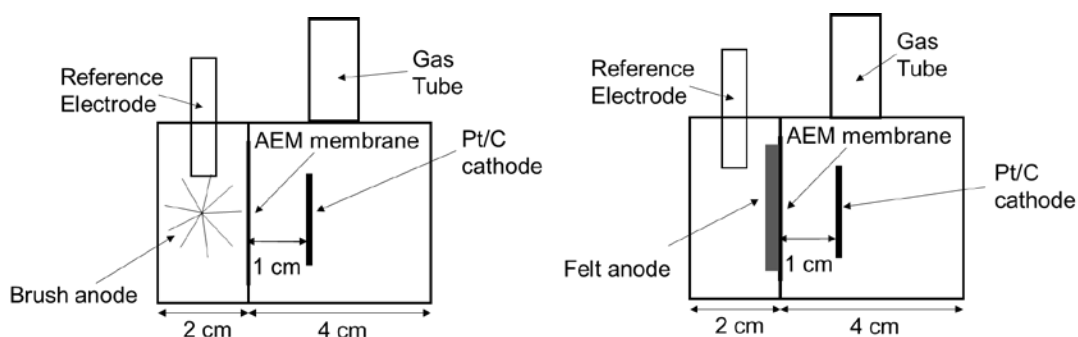


Figure 3-2: MEC configuration and anode placement in the anode chamber for the brush and felt anodes.

3.2.3 MEC operation

Two different electrolyte solutions were tested. Initially all anodes were acclimated in MFCs with sodium acetate fed reactor effluent as the inoculum and 2 g/L sodium acetate in 50 mM phosphate buffer solution (PBS, Na_2HPO_4 : 4.58 g; NaH_2PO_4 : 2.45 g, NH_4Cl : 0.31 g; KCl : 0.13 g in 1 liter of distilled water with mineral and vitamin solutions [10]) as the feed. The reactors were operated in a 30°C temperature controlled room in fed-batch mode with triplicate reactors for each anode type. Once steady potentials were reached and polarization tests were completed, the anodes were switched over to MECs with a 0.9 V applied potential using a power supply (BK Precision, USA).

New reactors were inoculated to increase the anolyte and catholyte conductivities to 100 mM PBS in MECs. The anodes were inoculated in MFCs with 50% wastewater and 50% 2 g/L sodium acetate in 50 mM PBS feed. Once the microbes were acclimated to 50 mM PBS feed, the conductivity was increased to 100 mM PBS (Na_2HPO_4 : 9.15 g; NaH_2PO_4 : 4.90 g, NH_4Cl : 0.31 g; KCl : 0.13 g in 1 liter of DI water with mineral and vitamin solutions). The microbes were acclimated once again, power was tested using polarization tests and anodes were moved to MECs.

The reactors were first tested with the same 50 mM PBS medium as used in MFCs for the anolyte, and 50 mM PBS as the catholyte. The pH was 7.1, the anolyte conductivity 8.1 mS/cm, and catholyte conductivity 6.7 mS/cm. The anolyte for the second set of reactors was the same as the MFC feed (2 g/L sodium acetate in 100 mM PBS) with a pH of 7.0 and conductivity of 12.1 mS/cm. The 100 mM PBS (Na_2HPO_4 : 9.15 g; NaH_2PO_4 : 4.90 g) catholyte had a conductivity of 10.9 mS/cm. Before each cycle the catholyte was sparged with high purity nitrogen gas (99.998%) for 10 minutes to remove oxygen creating an anaerobic system.

3.2.4 Measurements and Calculations

MFCs were acclimated using a 1000 Ω resistor in the circuit, and then polarization tests were conducted to obtain the maximum power. The brush MFCs with 50 mM PBS were tested using the single-cycle polarization test based on using different resistances over a single cycle. Due to the observation of power overshoot in preliminary tests, the power density of the felt was tested using a multiple cycle test, with a single resistance used for a complete cycle over multiple cycles [18, 52]. The multiple cycle polarization test was used to reduce the probability of power overshoot [52]. After acclimation of the anodes in MFCs with 2 g/L sodium acetate in 100 mM PBS, the power was tested using a single cycle polarization test for the felt reactors and a multiple cycle polarization test for the brush reactors (Fig 3-7). Reference electrodes were used to measure the electrode potentials (Ag/AgCl; model RE-5B, BASi, IN). A single reference electrode was used in the brush MFC reactor to measure both the anode and cathode potentials. The electrode spacing was much greater in the felt anode MFC reactors, so a different reference electrode measured the electrode potentials; one for the anode and one for the cathode (Fig.3-2b). The use of the two reference electrodes minimized the distance and solution resistance between the reference and measured electrode, resulting in a more accurate electrode measurement.

Current generation of the MECs was collected every 20 minutes using a multimeter (Model 2700, Keithley Instruments, Inc., OH) in circuit with a 10 Ω resistor. The average current density was calculated based on the current needed to recover 90% of the total charge normalized to the cathode surface area (I_{90} , A/m²) [22]. The gas in the gas bag and the cathode headspace were analyzed for hydrogen using a gas chromatograph (Model 8610B, SRI Instruments Inc., USA). Each time the gas was analyzed, the influent and effluent COD were monitored using standard methods (method 5220, HACH company, CO), and the pH and conductivity were measured using a probe and meter (Seven-Multi, Mettler-Toledo International Inc).

The measured volume of hydrogen (V_{H_2} , m³) was estimated using the gas bag method previously described [4]. The hydrogen production rate (Q_{H_2} , m³H₂/m³d) for each reactor was calculated as:

$$Q_{H_2} = \frac{V_{H_2}}{V_r \Delta t} \quad (1)$$

where V_r is the total volume of the reactor (m³) and Δt is the reaction time in days. The theoretical moles of hydrogen produced due to the current measured was calculated as:

$$n_{CE} = \frac{\int_0^T I dt}{2F} \quad (2)$$

where I is the current (A), F is Faraday's constant (96485 C/mole e⁻), and T is the total time. The percent of hydrogen recovered from the current, cathodic hydrogen recovery (r_{cat} , %), was calculated as:

$$r_{cat} = \frac{n_{H_2}}{n_{CE}} \quad (3)$$

where n_{H_2} is the amount of moles of hydrogen actually captured at the cathode [21]. Coulombic efficiency (CE , %) was based on the coulombic recovery (n_{CE}) divided by the theoretical moles of hydrogen dependent on substrate (n_{th}) [8]. The overall hydrogen recovered (r_{H_2} , %) was estimated as:

$$r_{H_2} = \frac{n_{H_2}}{n_{th}} \quad (4)$$

Energy recovery (η_E , %) was calculated as:

$$\eta_E = \frac{1.23}{E_{ps}} r_{cat} \quad (5)$$

where the maximum energy recovery is 1.23 V, the theoretical amount of energy to split water, divided by the applied voltage (E_{ps} , 0.9V). The COD removal (COD_{rem} , %) was calculated as:

$$COD_{rem} = \frac{\Delta COD}{COD_i} \quad (6)$$

3.3 Results and Discussion

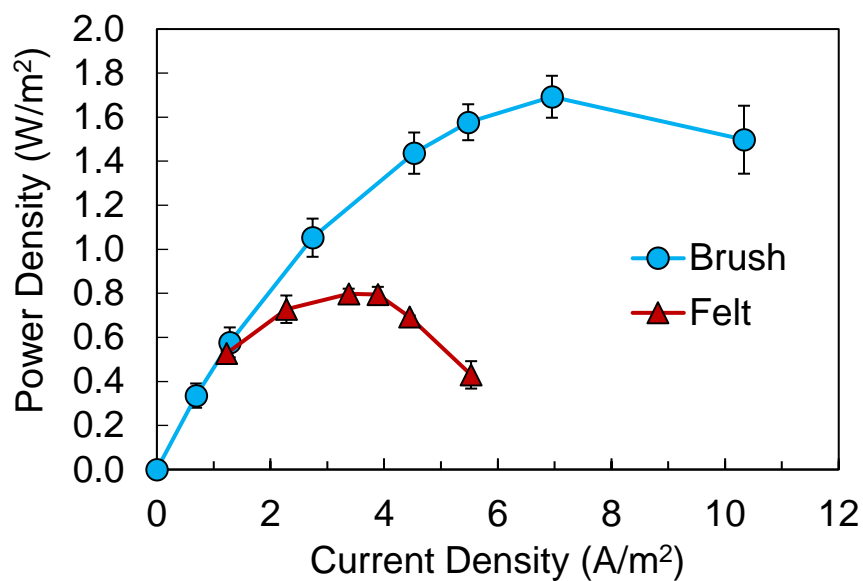
3.3.1 Power comparison for felt vs. brush anodes in MFCs with 50 mM PBS

The maximum power density using the felt anodes in MFCs with 50 mM PBS was 0.80 ± 0.02 W/m² (Fig. 3-3a). The brush MFCs had a maximum power density of 1.69 ± 0.10 W/m² (Fig. 3-3a). The brush MFCs had a higher power density than the felt anode MFCs, which was expected due to the lower electrode distance. While the cathodes for all reactors performed similarly, brush anodes had better potentials than felt anodes (Fig. 3-3b). The power density of the felt and brush MFCs could be affected by the varying electrode spacing and impacts due to ohmic resistance, but based on the measured electrode potentials, the felt anode potential was the limiting factor. The brush may have achieved a greater maximum power density because of its larger surface area for microbial growth [33]. It is unlikely that the felt anodes could perform better than the brush anodes in the MFCs due to the much larger spacing of the felt anode and cathode, which resulted in higher ohmic resistance. For example with a solution conductivity of 8.12 mS/cm, a current density of about 3.4 A/m², and an estimated distance between the anode and reference electrode (0.5cm), the decrease in anode potential was about 20 mV (Appendix, Equation 1). If the anode potentials were examined after removing the solution resistance from the comparison, the electrode potentials for the brush and anode become more similar, suggesting that the ohmic resistance was the main factor in the reduced power generation by the felt anodes compared to the brush anodes (Appendix, Fig 1).

3.3.2 Current densities and hydrogen recovery

After the anodes were transferred to MECs an additional voltage was added to the circuit, and the current was monitored. An example of the average current density for one cycle reveals that the felt and brush anodes resulted in differently shaped current profiles (Fig 3-4). The

(a)



(b)

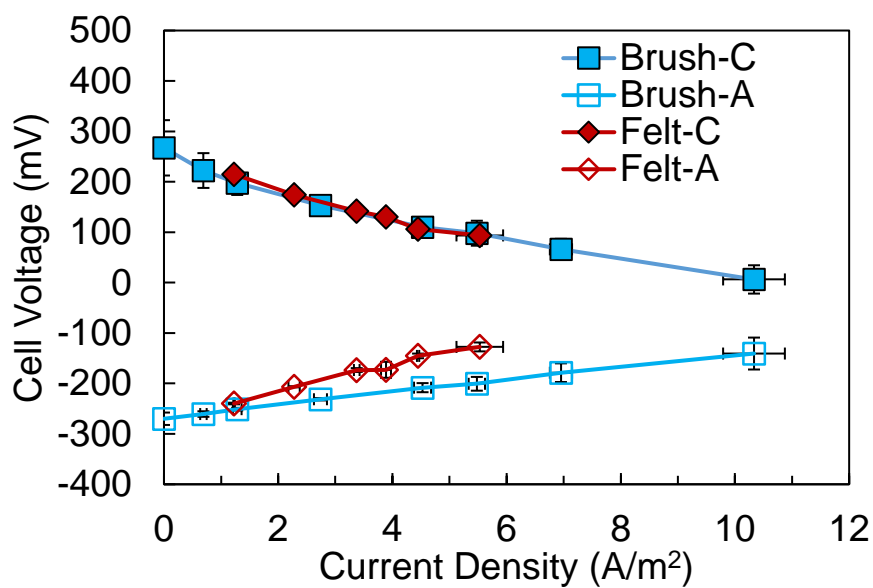


Figure 3-3: (a) MFC polarization tests using single-cycle (brush) and multi-cycle (felt) methods (b) Anode (A) and cathode (C) potentials.

brush had a plateau in current for about 40% of the total cycle time, where the felt initially showed a high peak in current, which then decreased continuously throughout the rest of the cycle. The average current density of the first 100 minutes for the felt anode MECs was 7.7 A/m²,

which was higher than that of the brush (5.9 A/m^2). The analysis of the current density based on the I_{90} analysis produced a different result (Fig. 3-5). The average brush I_{90} ($4.2 \pm 0.5 \text{ A/m}^2$) over the cycle (~ 24 hours) was higher than that of the MEC with the felt anode ($3.4 \pm 0.1 \text{ A/m}^2$), but both of these are lower than the current observed in the first 100 minutes. This means that initially the brush and the felt released more electrons at the beginning of the cycle, but while the brush reactors eventually produced a more constant current, the felt anode had a continuous decrease in current as time progressed.

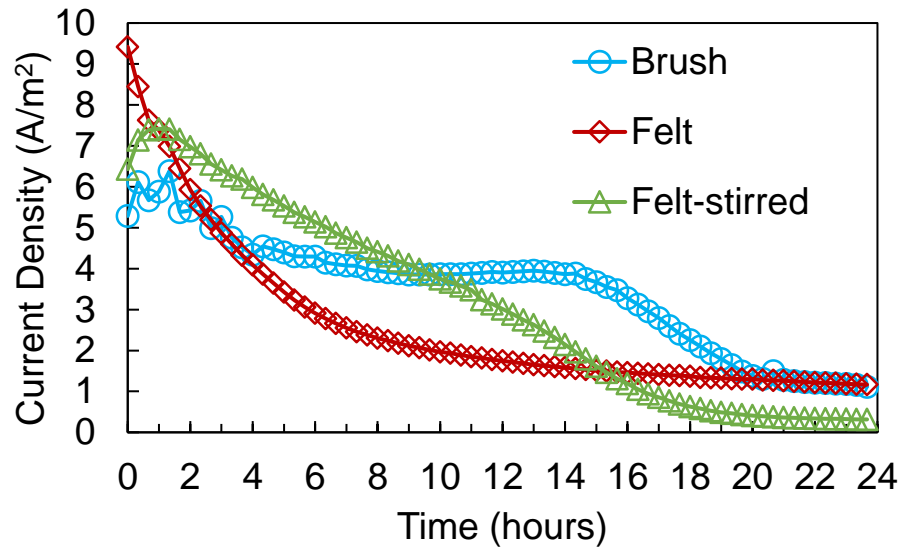


Figure 3-4: Example of average current density for one cycle of the MEC reactors.

To understand why the felt anode might produce a lower current over time, the impact of the electric field on the transport of the ions to the anode surface needs to be considered. The anolyte solution for the felt reactors was not within the electric field. This anode placement is important relative to ion transport. Ion transport with an electric field and molecular diffusion can be described by the extended Nernst-Planck Equation [43] as:

$$J_i = -D_i \nabla(c_i) - D_i \frac{z_i F}{RT} c_i \nabla(V) - D_i c_i \nabla(\ln \gamma_i) \quad (7)$$

where J is the chemical flux, i is the specific chemical species, c is the concentration, V is the potential, γ is the activity coefficient, T is the temperature, D is the diffusivity, R is the gas constant, and z is the charge of the species. This equation can be applied because the solution is not usually mixed in batch mode, so dispersion, advection and reaction forces are the only forces drawing the ions towards the anode. Since the solution was not in the electrical field, there was no force due to electric field in the felt anode chamber, so the flux of negatively charged ions to the felt anode was not possible. The brush was fully submerged within the solution making it possible for the ions from the solution to be transported to the microbes, and made the overall current more stable. The final pH of the catholyte for the brush anode MECs (8.7 ± 0.4) was greater than the felt anode reactors (8.0 ± 0.2) suggesting there was a higher hydrogen reaction evolution occurring, possibly due to the increased ion transport in the anolyte which allowed more electrons to be released by the anode.

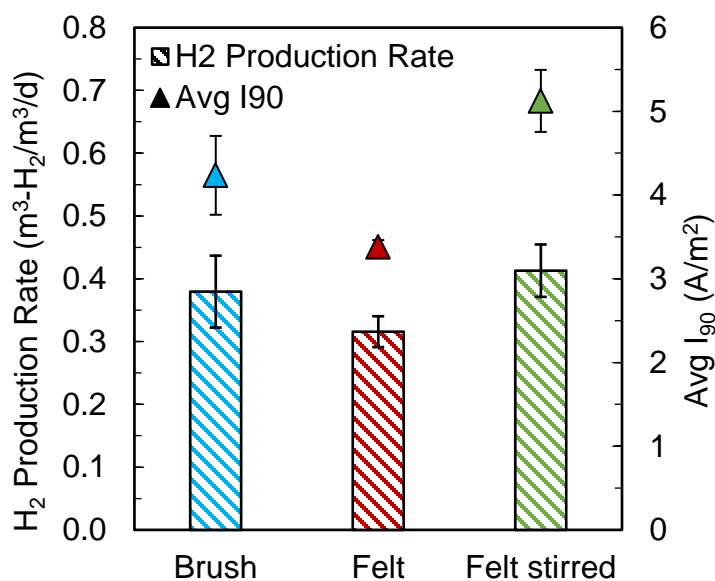


Figure 3-5: Average hydrogen production rate and average I₉₀ current densities for 50 mM PBS MECs.

Due to the higher overall current, the brush reactors also had a higher average hydrogen production rate of $0.38 \pm 0.02 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$ compared to $0.32 \pm 0.02 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$ for the felt reactors (Fig. 3-5). The higher hydrogen production rate for brush reactors was consistent with the higher average I_{90} current density.

3.3.3 COD removal, Cathodic and Hydrogen Recoveries, and Coulombic Efficiencies

The COD removal was lower for the felt MECs than the brush MECs, which supported the lower I_{90} and hydrogen production rate (Fig. 3-6). While the coulombic efficiencies were similar for all reactors, the cathodic recovery was higher for felt, resulting in a higher hydrogen recovery of $62 \pm 5\%$. The energy recovery was also larger for the felt reactors ($111 \pm 13\%$) than the brush reactors ($104 \pm 9\%$), but both values were larger than 100% indicating more energy was recovered than what was being applied as electrical power (i.e. not considering the energy in the substrate).

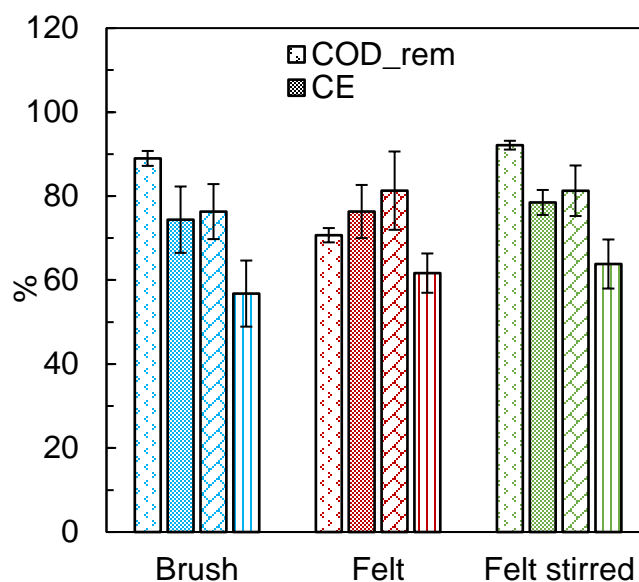


Figure 3-6: COD removal percentages, cathodic and hydrogen recoveries, and coulombic efficiencies for 50 mM PBS MECs.

Taken together, these results indicated that the felt MECs were able to produce the current needed to produce a reasonable amount of hydrogen, but lacked the ability to remove

COD. If a reduced anode spacing continues to be used, the mass transfer of the anolyte to the felt needs to be improved to enhance the performance of the felt anodes. Otherwise, the reactor configuration or electrode spacing needs to be reevaluated to increase the COD removal.

3.3.4 Benefits of stirring anolyte

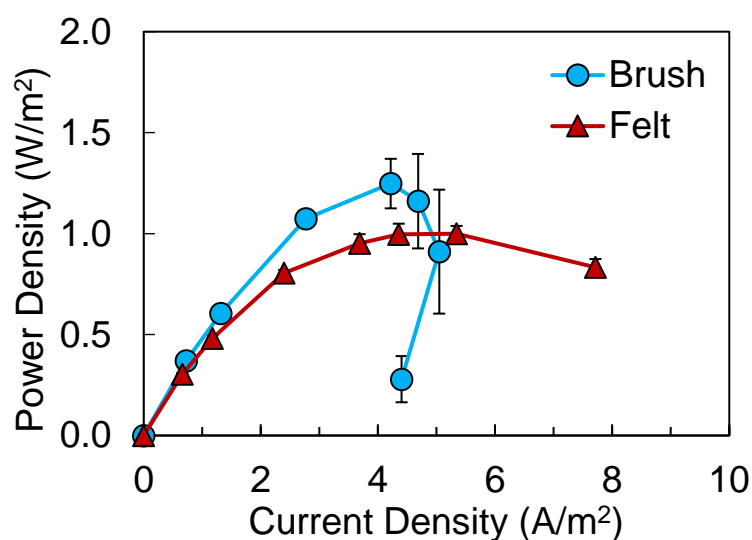
The high peak and rapid decline in current in the felt anode MECs suggested that current generation was limited by substrate transport to the felt anode. To test this hypothesis, the felt anolyte was stirred slowly. The anolytes for the brush anodes were not stirred due to the lack of space for a stir bar. While mixing in an MFC has been found to improve the rate of transport of substrate to the anode, it is an extra energy requirement and transfer of the oxygen from the cathode to the anode by stirring could adversely impact current generation by the anode [40]. Stirring the anolyte improved MEC performance by providing a higher average substrate concentration near the felt anode. The improved mass transfer was shown by an increase in the COD removal from $71 \pm 2\%$ (no stirring) to $92 \pm 1\%$ (stirring) for the felt anodes, although the coulombic efficiency, cathodic and hydrogen recoveries were not changed due to anolyte stirred (Fig. 3-6). While the current for the first 100 minutes in the example cycle was lower (7.2 A/m^2) (Fig. 3-4), stirring also increased the average I_{90} to $5.1 \pm 0.4 \text{ A/m}^2$ (Fig. 3-5). With an improved COD removal and higher I_{90} current, the average hydrogen production rate increased to $0.41 \pm 0.04 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$, which was higher than the production rate measured with the brush anodes (Fig. 3-5).

It is not clear whether these results could be translated to larger-scale reactors. If a larger reactor was operated with continuous flow, it would not be practical to stir the liquid inside a chamber [12]. The impact of flow past the anode during continuous wastewater treatment should be further examined to determine its impact on current generation using flat anodes.

3.3.5 MFC operation with a 100 mM PBS electrolyte

The effect of solution conductivity on MFC performance was determined by acclimating the reactors to a 100 mM PBS electrolyte and conducting polarization tests. Single-cycle polarization tests were conducted for the felt anode MFCs, and a multiple-cycle was done for the brush anode MFCs to try to avoid power overshoot (Figure 3-7). Usually the use of a multiple cycle polarization test, where a different resistor is used for each cycle, avoids power overshoot [52]. However, power overshoot was still observed for the brush MFCs with 100 mM PBS. A

(a)



(b)

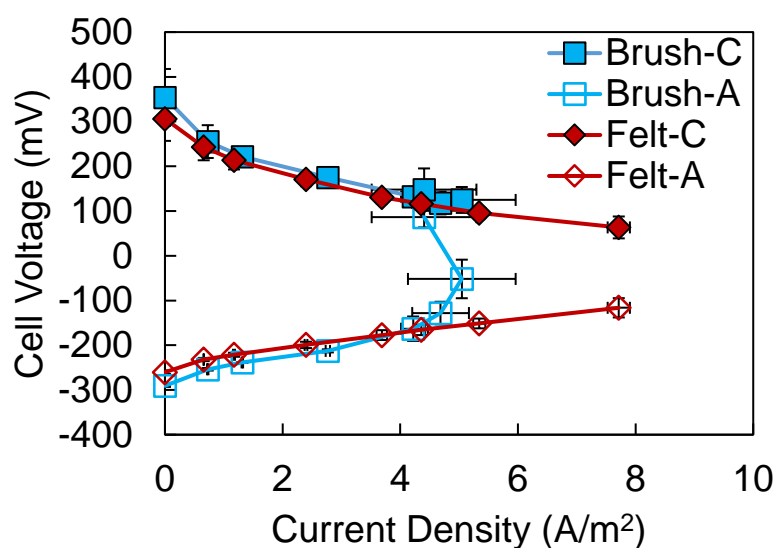


Figure 3-7: (a) MFC polarization tests with 100 mM PBS using single-cycle (felt) and multi-cycle (brush) methods (b) Anode (A) and cathode (C) potentials.

wipe separator was added between the anode and the cathode to ensure that the brush anode was not touching the cathode, but this did not avoid power overshoot either. The result of power overshoot was that the brush reactors produced a lower maximum power density (1.25 ± 0.12 W/m²) than the reactors with 50 mM PBS. However, the results with the felt anode reactors was different, as they produced a higher maximum power density of 1.00 ± 0.04 W/m². This increase in power is consistent with that expected when the solution resistance is reduced [53]. However, the lack of an increase using the brush reactors was likely due to power overshoot, indicating the anodes could not continue to produce higher current despite the reduced solution resistance.

3.3.6 MEC operation with a 100 mM PBS electrolyte

The felt and brush anodes were transferred from MFCs to MECs and further examined for hydrogen gas production using the 100 mM PBS electrolyte. Consistent with MFC tests, the average I_{90} current density (3.9 ± 1.6 A/m²) did not increase for the brush anode MECs, nor did the hydrogen production rate (0.37 ± 0.10 m³H₂/m³d) (Fig. 3-8). For the MECs with felt anodes, the hydrogen production rate and I_{90} current densities slightly increased to 0.40 ± 0.04 m³H₂/m³d and 3.7 ± 0.4 A/m² (Fig. 3-8). The current density was still lower than observed when the anolyte was stirred in the felt anode chamber with the 50 mM PBS electrolyte, but the hydrogen production rate was similar. Solution conductivity was beneficial for hydrogen production, but did not increase the current transferred in the MECs.

The COD removal also slightly increased for the felt anode chamber, which suggested that the diffusion resistance decreased with solution conductivity (Fig. 3-9). When compared to the COD removal when the felt anolyte solution was stirred with 50 mM PBS, the removal was not as high. The lower COD removal indicates that a more turbulent flow would assist in the removal of COD for a substrate with higher solution conductivity. The brush MECs instead had a

slight decrease in COD removal, which could be due to a varied microbial community from a higher salinity feed (Fig. 3-9).

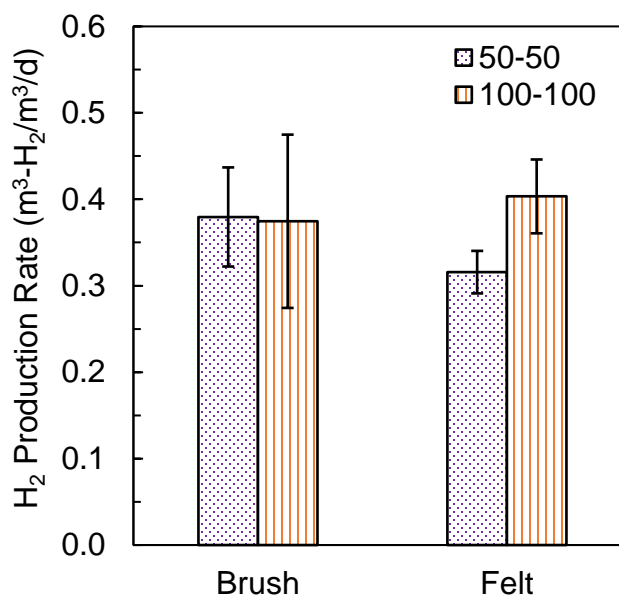


Figure 3-8: The comparison of the hydrogen production rate for MECs with 50 mM PBS and 100 mM PBS as the base for the anolyte and catholyte.

The energy recovery did not change in either the brush or felt MECs (Fig. 3-9). The amount of energy recovered from the MECs were similar to that produced when 50 mM PBS was used. All of these results on hydrogen production rate, current density, and energy recoveries suggest that with this reactor configuration, the higher solution conductivity does not enhance performance. The lack of improvement could be due to the small electrode distance (1-1.5 cm) and an already minimized solution resistance [10], or for the case of the brush anodes, a negative effect on the microbial community due to oxygen and phosphate [6] from the initial MFC acclimation. Oxygen could have affected the number of anaerobic microbes that have the capability to produce electricity, or the high phosphate has been shown to adversely affect a commonly found microbial species in MECs [6,12]. If the electrode distance is large, like what

could be seen in a larger reactor, a higher solution conductivity could still be beneficial, but acclimation should be completed in MECs to assure no harm from oxygen.

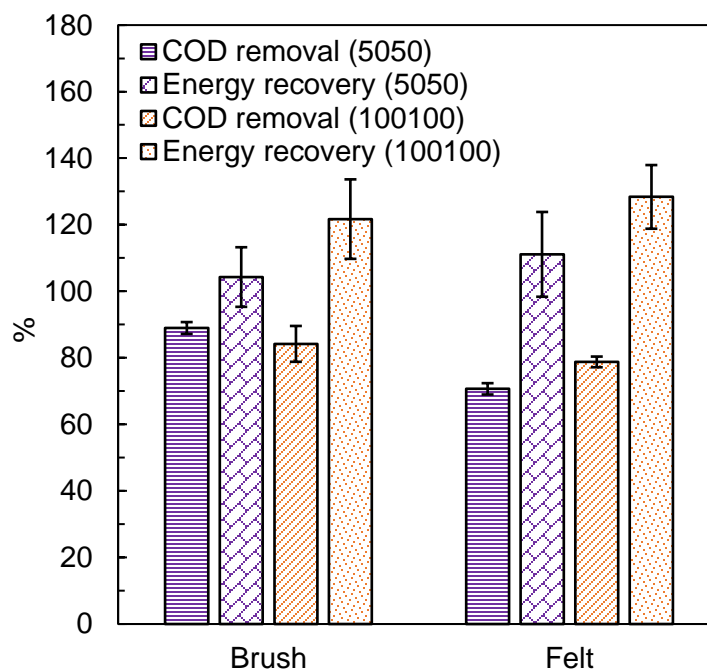


Figure 3-9: COD removal and Energy recovery comparison for MEC reactors with 50 mM PBS and 100 mM PBS.

3.4 Conclusions

MECs with brush anodes showed better hydrogen production than those with flat felt anodes in fed-batch tests in a 50 mM PBS electrolyte. However, when the anolyte solution was mixed, the felt anode MECs ($0.41 \pm 0.04 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$) had improved and slightly higher hydrogen production rates than MECs with brush anodes. The improved performance of the felt anodes in MECs with stirring suggested that current generation was limited by substrate transport to the felt anodes. This substrate limited transport, and a lower current density without stirring, also reduced the extent of COD removal. However, with stirring and improved mass transfer of acetate to the biofilm, COD removal was increased. As stirring is not practical for larger-scale MEC operation,

and increases the energy requirements for operation, it is concluded that brush anodes would provide better performance than felt anodes for MECs.

Solution conductivity was increased in order to decrease the amount of ohmic resistance within the reactors. However, the MECs with brush anodes did not have improved performance likely due to an adverse impact of the higher phosphate concentrations on the microbial anode communities. MECs with felt anodes reactors and 100 mM PBS had a hydrogen production rate comparable to that of the stirred felt MECs ($0.40 \pm 0.04 \text{ m}^3\text{H}_2/\text{m}^3\text{d}$), although the average current densities over the cycle did not improve. These results suggest that when deciding on anode materials for large scale MEC application, diffusion rates and COD removal need to be considered, and when applying a reduced spaced electrode architecture with high solution conductivity, the anodes should be directly acclimated in MECs.

Chapter 4

Future Work

To improve our understanding of MEC reactor configuration, flat anode performance, and increase in solution conductivities, additional research should be conducted.

- Examine whether felt anode performance could be improved by moving the location of the felt anode in the reactor, so the anolyte is in the electric field, but the electrode spacing is still small.
- Examine felt anode performance under continuous flow conditions. A high recycle rate may be required to minimize substrate limitations and see an improved performance.
- If the continuous flow does not improve the COD removal alone, a spacer should be added to make flow more turbulent and better mimic the mixing in small reactors.
- Evaluate hydrogen production rates with ultrathin anode and cathode chamber volumes with various flows.
- Determine if longer acclimation times of the anodes to higher salt concentrations could improve their tolerance to the higher salt concentrations. The advantages of a reduction in ohmic resistance to current generation cannot be realized unless the anode biofilm can tolerate the higher salt concentrations.

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Appendix

Supplemental Information

Estimating ohmic resistance from solution conductivity. The solution ohmic resistance per unit length, or R_{Ω}/l (Ω/cm), obtained from the measured solution conductivity (σ , mS/cm), as

$$\frac{R_{\Omega}}{l} = \frac{10^3}{\sigma A} \quad (1)$$

where A is the cross-sectional area (7 cm^2), and 10^3 is for unit conversion [$(\text{mS}/\text{cm}) = 10^3/(\Omega \text{ cm})$].

Corrected electrode potentials for felt. Note that the actual ohmic resistance can only be measured using EIS if the reference electrode is in the electric field (i.e. between the anode and cathode) [56]. Otherwise, a current interrupt method can be used to measure the cell ohmic resistance. The ohmic resistance estimated from the solution conductivity is expected to underestimate slightly the actual ohmic resistance as this approach does not include the actual electrode surface solution resistance.

Instead of estimating the cathode potentials based on a single reference electrode, 2 reference electrodes were used, one for the anode (REa) and one for the cathode (REc) due to the larger electrode spacing. The current-dependent corrected anode (E_{AnREa} , mV) and cathode potentials (E_{CatREc} , mV) were obtained by

$$E_{AnREa} = E_{An} - \left(\frac{10^3 R_{\Omega} d_{An-REa}}{l} \right) i \quad (2)$$

$$E_{CatREc} = E_{Cat} + \left(\frac{10^3 R_{\Omega} d_{Cat-REc}}{l} \right) i \quad (3)$$

where d_{AnREc} is the distance (cm) between the anode and the anode reference electrode, E_{Cat} is the measured cathode potential, and d_{CatREc} is the distance between the cathode and the cathode reference electrode.

Corrected electrode potentials for brush. For MFCs with a smaller electrode spacing, only one electrode is needed to estimate the anode and cathode potentials. Equation 2 can be used to calculate the corrected anode potential based on the distance between the reference electrode and the anode. Usually

the cathode potential is calculated using the anode potential, but this would not take into account the ohmic resistance. Instead to calculate the corrected cathode potential, the current-dependent whole cell ohmic loss that reduced the cell voltage should be added to the cathode potential, based on the distance between the electrodes (d_{An-Cat}), we used

$$E_{Cat,U+AnRE+IR} = U + E_{An,RE} + \left(\frac{10^3 R_{\Omega} d_{An-Cat}}{l} \right) \quad (4)$$

where $E_{an,RE}$ is the corrected anode potential, and U is the measured whole cell potential.

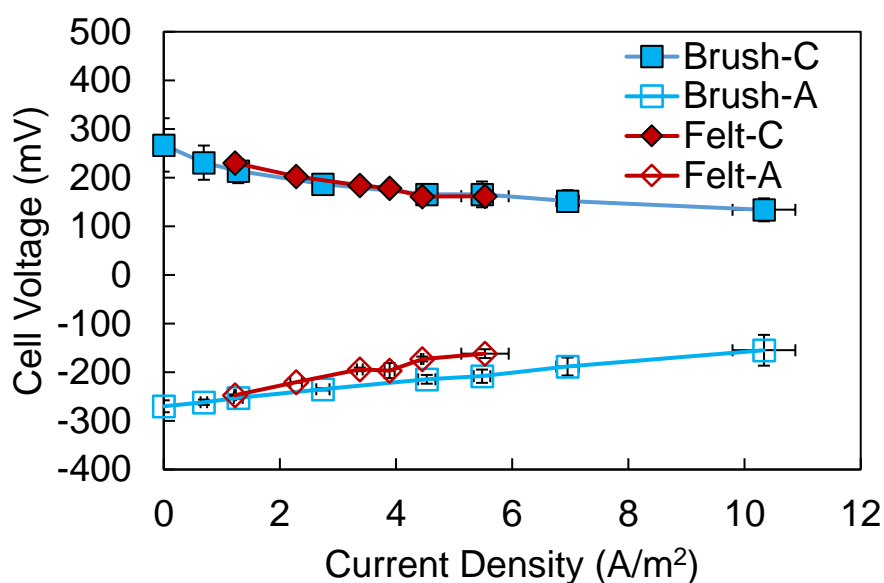


Figure A-1: Corrected anode (A) and cathode (C) potentials for the 50 mM PBS reactors using equations 2 and 3 for the felt and 4 for the brush reactors.