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Comparative evaluation of the performance of platinum and activated carbon as catalyst in microbial fuel cells for the energy integrated treatment of brewery wastewater

The objective of microbial fuel cells (MFC) is the biological treatment of wastewater and simultaneous generation of bio-electricity. Catalyst coated membranes can account for up to 70 % of large-scale MFC costs; therefore, to increase the commercial attractiveness of the technology, it is inevitable that the catalyst is cost-efficient with acceptable catalytic performance. We have performed in-situ measurements in an air-breathing single chamber MFC to compare the electrical power generation using platinum and activated carbon coated membranes. Coulombic efficiencies of 14.5 % and 11.6 % were recorded for the platinum and activated carbon ORR catalysts, respectively and 53 % COD removal using brewery wastewater as bio-fuel. The results suggest that activated carbon can replace platinum-based catalysts without a significant loss of performance. This can be a significant cost saving solution (up to 15 times) for large scale and commercial MFCs, especially when biological treatment of industrial wastewater, such as brewery wastewater, is the primary objective.

Descriptors: brewery wastewater treatment, microbial fuel cell (MFC), oxygen reduction catalysts, coulombic efficiency

1 Introduction

For the biological treatment of industrial wastewater (such as brewery wastewater) using conventional technologies, energy between 1.8 – 6.8 kJ/L is required [1, 2]. Most of the energy demand (> 60 %) is due to the aeration process [3]. It has however been shown that the chemical energy contained in wastewater in the form of organic matter can be as high as 35 kJ/L [4, 5]. That means, an energy positive (or at worst, energy neutral) biological wastewater treatment can be achieved by; 1) eliminating the energy intensive aeration process of conventional wastewater treatment and 2) harvesting the energy content of the wastewater stream and integrating it back into the wastewater treatment balance of plant (BoP).

The microbial fuel cell (MFC) is one technology that can remove the organic matter content from wastewater while simultaneously converting the same to electrical energy without the need for active aeration. Recent studies have shown that energy self-sufficiency in biological wastewater treatment is indeed achievable with the MFC technology [6, 7]. Recent review and studies have shown the benefits and feasibility of the MFC replacing conventional methods in the biological treatment of industrial wastewater, especially brewery wastewater [8, 9].

A typical MFC makes use of exoelectrogenic microorganisms as biocatalyst to oxidize the organic matter in the anode half reaction, releasing electrons and protons in the process. The electrons travel through an external circuit (generating electrical current) to the cathode side, figure 1A. The protons travel through a proton permeable membrane to the cathode side, where they recombine with the electrons and electron acceptors (typically oxygen) with the help of an oxygen reduction reaction (ORR) catalyst to form H_2O. The activity of the biocatalyst on the anode determines the chemical oxygen demand (COD) removal (wastewater treatment) efficiency, while the activity of the ORR-catalyst on the cathode side largely controls the electrical power generation efficiency, which is referred to as the coulombic efficiency (CE). The ORR-catalyst is therefore a critical component for achieving high electrical energy conversion efficiency.

As in other established fuel cell types such as polymer electrolyte membrane fuel cells (PEMFC), state-of-the-art MFCs commonly use platinum-based materials as ORR-catalyst [10] because of the inherent catalytic properties of platinum. However, platinum has the double disadvantages of high cost and low availability [11]. Especially for large-scale applications, it has been shown that about 70 % of the capital cost of an MFC is due to the use of platinum-based ORR-catalysts [12]. Thus, in order to cut investment costs and improve the market attractiveness of the MFC technology, it

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is imperative to seek for alternatives to platinum without significant loss of electrical conversion efficiency. As [13] suggested, ideal ORR-catalysts should be highly active, easily available, durable, scalable and cost efficient.

Platinum group metal-free catalysts such as CoTMPP [14] and iron phthalocyanine (FePc)-MnO_x composite [15] have already been tested as alternatives to platinum. It was determined that in order to achieve a performance comparable to that of platinum based ORR catalyst, much higher loading of such non precious metal ORR catalyst is required, resulting in increased overall costs [16].

High surface area materials such as graphite granules and activated carbon are promising alternatives to metal based ORR-catalysts [17]. Moreover, it has been reported [18] that, these can be up to 15 times more cost efficient than their metal based counterparts.

Zhang et al. [19] already achieved comparable performance to platinum using activated carbon catalyst cold-pressed on a nickel mesh current collector (diffusion layer). They attributed the high performance of the activated carbon cathode to the high surface area of the ORR-catalyst, combined with the high electrical conductivity of the nickel mesh. However, the use of nickel mesh as current collector/diffusion layer presents an additional cost factor. In another study [20], activated carbon blended with 10 % carbon black achieved better power density than platinum. In that work, stainless steel mesh was used as support for the carbon black/activated carbon mixture, and as the diffusion layer. The performance of the activated carbon on carbon black ORR-catalyst was 7 % higher than that of platinum even after 5 months of operation, suggesting good durability and stability. The results were attributed to the electrical conductivities of the carbon black and stainless steel mesh, as well as the high activated carbon loading, which was 86 times more than the platinum loading.

It therefore, becomes interesting to investigate the power generation performance and durability of activated carbon as ORR-catalyst compared to platinum, when they both have the same loading and without the use of high electrically conducting metal mesh as support structure. To this effect, [21] tested the performance and long term stability of activated carbon using only carbon paper as the support structure and the gas diffusion layer. They found that the highest performance was achieved within the initial stages and then dropped by up to 55 % over the next months. The decrease in performance losses was attributed to mass transport resistance in the catalyst support structure. The mass transport over-potential increases the overall cell internal resistance, which also increases with time.

One way to avoid the mass transport limitation is to coat the ORR-catalyst directly on to the membrane to form a single structure, herein after, referred to as the catalyst coated membrane (CCM). The use of a CCM makes it possible to operate the MFC without the need of a gas diffusion layer.

Thus far, ORR-catalyst related studies in MFCs have mostly been focused on the synthesis and effects of loading and catalyst support on cell performance. Moreover, they have often been limited to laboratory settings where real wastewaters are substituted by model solutions, such as acetate solution [13, 22]. It is convenient to use model solutions in laboratory studies because they provide high COD values, favorable pH-values and electrolyte conductivity. Such studies however, do not consider some of the complexities related to the use of real wastewater, such as low COD content, low pH-value, and performance losses due to an increase in the cell ohmic resistance from the clogging of the porous matrix of the anode electrode [23].

In this work, we have investigated the performance of a 1-litre air-breathing microbial fuel cell using either platinum or activated carbon CCMs with equal loadings (0.5 mg/cm²) and without the use of a catalyst support structure (gas diffusion layer). We will evaluate the extent of the electrical power losses and stability if standard Pt coated membrane was replaced with activated carbon coated membrane with equal loadings in the MFC for the treatment of brewery wastewater. Activated carbon coated membranes have the advantage that they can be up to 15 times cheaper than the Pt coated membranes. Therefore, the use of activated carbon will be more favorable for costs saving during upscaling and for the commercialization of industrial scale MFCs. Hence,

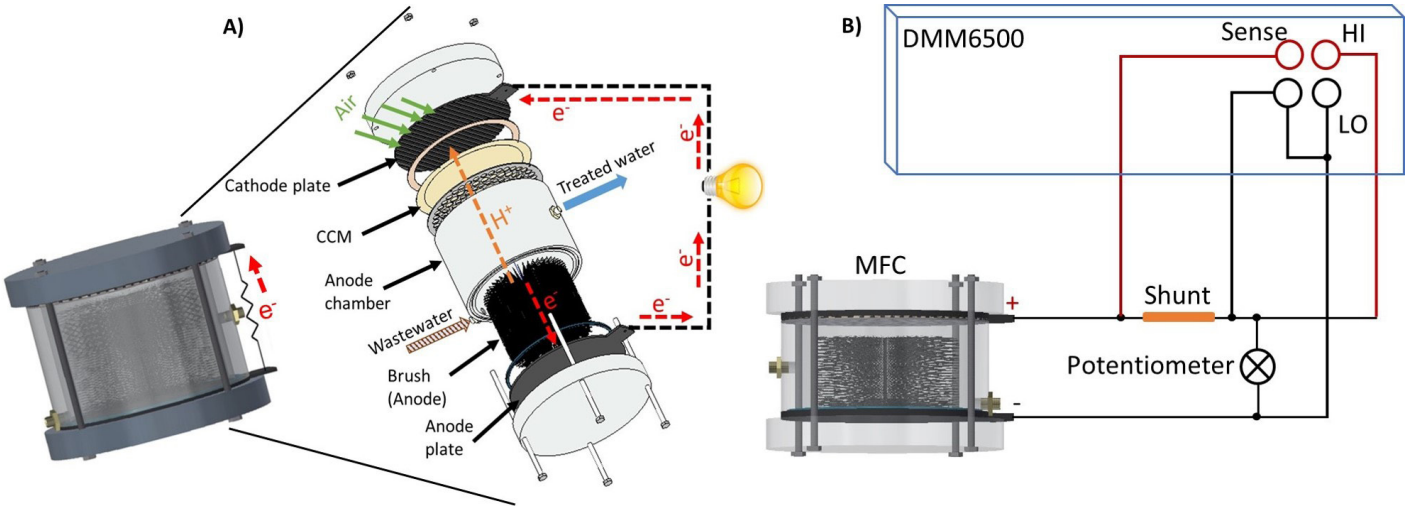

Fig. 1 **a) Test cell design and components b) Set-up of the DMM6500 digital multimeter for the simultaneous measurement of electrical current and voltage**

the objective of this work is to improve the cost effectiveness of an MFC without compromising its power generation efficiency, durability and stability.

The evaluation and comparison of the performance of the ORR catalysts have been done in terms of the generated power densities, the evolution of electrical currents under stress condition and the resulting coulombic efficiencies. The efficiency of the wastewater treatment was determined by the COD removal efficiency.

There already exists a number of studies on the application of Pt and activated carbon in MFC [24, 25]. Nevertheless, this is the first time that catalyst coated proton exchange membranes (coated with Pt and activated carbon with equal loadings) have been tested and compared in-situ, in the same cell set-up and without the use of an electrically conducting catalyst support structure, using brewery wastewater as the bio-fuel source.

2 Materials and Methods

2.1 Cell design and major components

The 1-litre (anode) single chamber MFC used was previously described in [23] and a sketch is shown in figure 1A. In order to ensure high surface area for biomass growth and to prevent pore blockage, a graphite brush instead of a porous matrix was used as the anode electrode. The custom-made brush manufactured by Bürsten-Baumgartner OHG (Germany) has a diameter of 100 mm and about 1800 fibers with each fiber having a diameter of 0.3 mm, giving an active anode surface area of about 0.018 m². Impregnated gas tight graphite plates (Müller & Rössner GmbH und Co. KG, Germany) were used as current collectors for both the anode and cathode half-cells. The cathode current collector had machined parallel channels to ensure the free flow of air to facilitate the ORR.

A proton permeable perfluorosulfonic acid (PFSA) membrane (~ 240 µm thick) separates the anode half-cell from the cathode half-cell. The side of the membrane that faces the cathode half-cell is coated by hot-pressing with the ORR catalyst (either Pt or activated carbon). The membrane in combination with the ORR catalyst is referred to as catalyst coated membrane (CCM). Each of the CCMs (one with Pt and the other with activated carbon) had an active surface area of 113 cm² and a catalyst loading of 0.5 mg/cm². Both CCMs were manufactured and supplied by FUMATECH BWT GmbH, Germany. The CCMs that are reputable for high performance, reliability and durability are mostly used for the more established fuel cell types such as PEMFC, AFC, and PEMEC etc. [26]. They are also scalable and favorable to industrial applications.

Table 1 Medium characteristics

Parameter	Acetate solution	Brewery wastewater
COD [mg/L]	4735	2191
pH	7.2	6.8
Temperature [°C]	19.5	19.5
Electrical conductivity [µS/cm]	906	364
Redox potential [mV]	– 36	– 65

2.2 Acetate medium, brewery wastewater and anaerobic sludge preparation

The acetate medium was prepared according to the protocol reported in [23]. The brewery wastewater was collected from the equalization tank of the wastewater treatment facility of the brewery "Freiberger Brauhaus" in Freiberg, Germany. In order to eliminate any other microbial community in the wastewater that could compete with the exoelectrogenic bacteria in the sludge and to preserve the physico-chemical characteristics (Table 1) of the sample over time, the brewery wastewater sample was autoclaved at 121 °C and 2 bar for 30 minutes, immediately after its collection. The brewery wastewater used throughout the study was from the same initial collection batch (sample), and was used without dilution.

The exoelectrogenic microorganisms, which were allowed to grow on the brush during the inoculation phase, naturally exists in activated sludge that was collected from the municipal wastewater treatment plant in Freiberg, Germany. The watery sludge was separated by cloth filtration into a filtrate and a concentrate. Both fractions were separately mixed with acetate solution and their ability to grow microorganisms on the brush were analyzed ex-situ by determining the COD degradation activity. The inoculated activated sludge to medium ratio was 1 : 20.

2.3 Experimental procedure and measurement techniques

The experimental investigation was structured into three phases. Phase 1 (inoculation and acclimatization period) was for the growth of the biomass on the graphite brush using sodium acetate medium as carbon source. The COD levels, pH-values, the electrical conductivity and the evolution of polarization and power density curves were measured during 18 days of continuous operation. In phase 2, the acetate solution was replaced by brewery wastewater as carbon source for 14 days while measuring and monitoring all the electrical (voltage and electrical current) and physico-chemical parameters (temperature, pH-value etc.). In phase 2, the external resistance at which the MFC achieved maximum power density was recorded. In phase 3, the CCMs were tested under stress condition for 14 days, whereby, the cell was operated in steady state at the external resistance corresponding to the maximum power density obtained in phase 2.

The MFC was operated in fed-batch mode during all phases of the investigation. A peristaltic pump, BT100-1F with peristaltic pump head YZ1515X (both from Longer Precision Pump Co. Ltd) was used to maintain medium circulation in a closed loop within the MFC anode chamber at a flowrate of 7 mL/min. This was necessary to ensure adequate mixing within the chamber.

The organic matter content (COD) of the solution was measured by photometric tests using the Lasa 100 device and LCK 014 cuvettes, both from Hach Lange GmbH, Germany. The electrical conductivity was measured using the WTW LF 325 device while the pH-value and redox potential were both measured using the

Hach Sension 378 device. The physico-chemical parameters of the electrolyte were measured at the start of each phase and monitored on a daily basis afterwards.

DC current and voltage measurements were performed using the Digital Multimeter device Keithley-DMM6500. Typically, this single parameter device can only measure one DC parameter at a time. However, in the testing of MFC, it is necessary to measure all electrical parameters (DC voltage, current and external resistance) simultaneously. In order to achieve this, a small shunt resistor (~ 1 Ohm) was connected in series to the digital multimeter, as shown in figure 1B. To serve as the potentiometer, a variable resistor (RV20N, from Tokyo Cosmos Electric Co. Ltd) was connected to the system as shown in figure 1B. With the variable resistor, the external resistance of the MFC system could be manually tuned from 0 – 18 kΩ.

During phases 1 and 2 of each experiment, polarization curves were measured once every day by changing the external resistance from 18 kΩ to 0 Ω while recording the resulting DC current and voltage and then plotting the cell voltage against the DC current density. From the DC voltage and current, the power density was calculated according to Equation 1. In phase 3 (stress test), the external load was set to the resistance corresponding to the maximum achieved power density in phase 2 and the MFC was operated for 14 days continuously while recording the generated DC current. In total, each CCM had a continuous operation time of 46 days over the three phases.

2.4 Key Performance Indicators

The major factors that were considered to characterize the MFC performance are the power density generation, the coulombic efficiency and the COD removal efficiency. Since the investigation is focused on the ORR catalyst, the generated DC currents were normalized to the cathode active area. Therefore, the power density was calculated according to:

$$Power\ density = \frac{I * U}{A_{cathode}} \qquad \text{(Eq. 1)}$$

where $A_{cathode}$ is the active surface area of the cathode, in this case, 113 cm², I is the absolute DC current and U is the DC voltage.

The coulombic efficiency (CE) gives an indication of the energy conversion efficiency of the MFC. It relates the electrical charges released from COD degradation in the anode to the charges effectively converted to electrical current in the cathode. The CE was calculated using the following equation:

$$CE = \frac{M_{O_2} * \int_0^t I dt}{F * n * V_{anode} * \Delta COD} \qquad \text{(Eq. 2)}$$

where, M_{O_2} is the molar mass of molecular oxygen, F is the Faraday constant and n is the number of electrons consumed when O_2 is reduced to $2O^{-2}$. V_{anode} is the total volume of the MFC anode chamber, in this case 1 liter; ΔCOD is the the change in COD content over time and I is the corresponding DC current generated over time.

The COD removal efficiency was calculated based on the measured initial and final COD content.

$$COD\ removal\ = \frac{COD_{initial} - COD_{final}}{COD_{initial}} \qquad \text{(Eq. 3)}$$

3 Results and Discussion

3.1 Wastewater treatment performance

As mentioned in section 2.2, the sludge filtrate and concentrate were tested ex-situ prior to inoculation in phase 1. About 51 % COD removal was achieved with the sludge concentrate compared to only 7.8 % with the filtrate after 14 days of pre-testing (Fig. 2). Consequently, the sludge concentrate was used for all subsequent phases of the investigation.

Figure 3 (see page 22) shows the COD profiles and treatment efficiencies when sodium acetate solution was used as carbon source (phase 1) and when brewery wastewater was used as carbon source (phase 2). A steady increase in the COD removal efficiency was observed for both fuel sources. During phase 1, a significant COD degradation (18.5 %) was already observable by day 2, meanwhile, in phase 2, only 0.7 % COD degradation was recorded over the same period of time. We attribute this to the much higher COD content in the sodium acetate solution in phase 1 (4735 mg/l) and the time needed by the microorganisms to recover from temporary starvation during the change of medium from phase 1 to phase 2. The recovery from temporary starvation of the exoelectrogenic bacteria also explains the increase in the COD removal in phase 2 between day 2 and 3. By day 4, the COD removal efficiencies were quite comparable at 23.7 % (phase 1) and 26.6 % (phase 2) respectively.

The COD removal efficiency continued to increase in phase 2 to 50.3 % on day 12 (compared to 40 % at the same stage in phase 1), indicating that the microbial activity was still strong and that the microbial community was still growing. Experiments in phase 2 lasted for 14 days because the subsequent low COD values (< 500 mg/l) could lead to starvation of the microorganisms, which could in turn

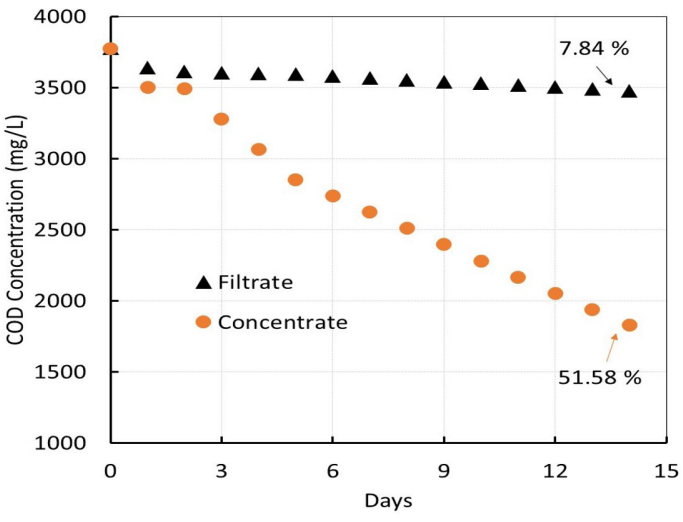

Fig. 2 COD removal efficiency of activated sludge components

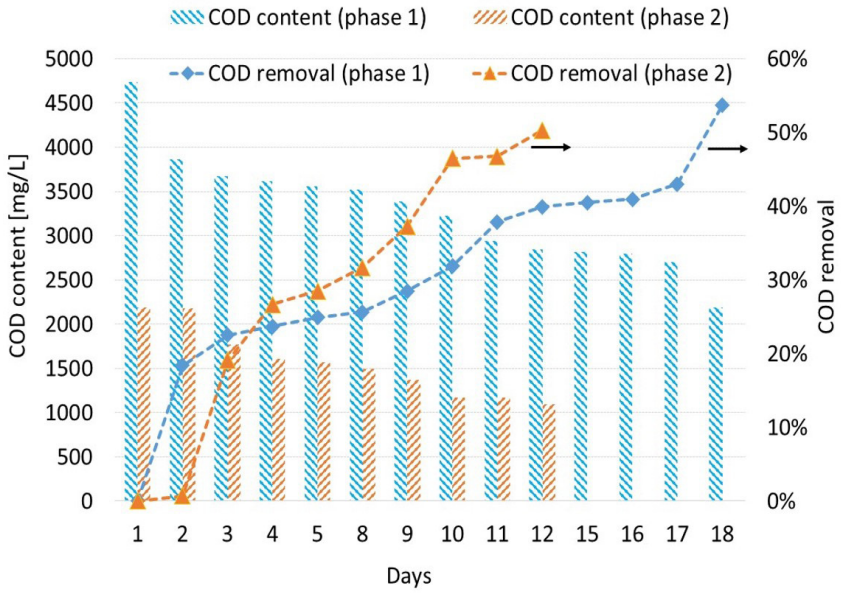

Fig. 3 COD content and removal efficiency during phase 1 (using acetate solution and activated carbon CCM) and phase 2 (using brewery wastewater and activated carbon CCM)

affect the results in phase 3. As the starting COD values were quite high, (4700 mg/l in phase 1 and 2200 mg/l in phase 2) and the focus of this work was on the cathode catalyst activity, it was important to make sure that the COD values did not get below a threshold that they may become limiting to the overall cell performance.

The average COD removal efficiency achieved over phases 1 and 2 was 53 %. Although this is much lower than values that have been reported (> 90 %) with anaerobic sludge after pre-screening of the biomass cluster, it is well within the range of reported wastewater treatment efficiencies when unscreened sludge from municipal wastewater treatment facility was used. For example, [27] reported COD removal efficiency of 79 % and [28] achieved 40.3 % after 45 and 20 days of operation respectively, using sludge from communal wastewater treatment plant with unknown biomass composition.

The COD removal trend and efficiency was identical with the use of the Platinum and activated carbon coated CCMs for both phase 1 and phase 2. This was however, expected, since the water treatment efficiency is controlled by the activity of the biocatalysts and not the ORR electro-catalyst.

3.2 Cell polarization

Figure 4 shows the evolution of DC voltage and current density characteristics (polarization curves) during the inoculation and stabilization phase, phase 1. During this phase, one polarization curve was recorded each day. It can be seen that the performance increases steadily during the first 14 days of operation, reaching a maximum current density of 0.015 mA/cm² and a thermodynamic cell voltage of 458.5 mV. This is significantly lower than the theoretically maximum attainable MFC voltage of 800 mV [29] under similar but not identical physico-chemical conditions such as temperature, pH and oxygen concentration in the cathode. The low thermodynamic voltage is due to losses within the cell that are mostly related, but not limited to design, operation and material properties. However, it does not have any effect on this comparative study, since both CCMs were subjected to the same conditions and they recorded comparable thermodynamic voltages.

No significant improvement of the polarization performance could be seen from the 14th to 17th day of operation, suggesting that the cell had reached full stabilization. During this stabilization period (typically at very low current densities), the activity of the microorganisms on the anode side and the catalyst on the cathode side have a dominant effect on the electrical current output, and this is the activation controlled stage. By day 18, there was a decrease in the electric current generation performance, compared to day 14, as can be seen from the polarization curves. Even though the cell activation for days 14 and 18 were quite comparable, ohmic losses were higher on day 18. Ohmic losses refer to all overpotentials resulting from the resistance to the flow of ions (through the electrolyte and membrane) and electrons (through the electrically conducting cell components). The ohmic losses are characterized by a straight line on the polarization curve and are typically dominant at mid-range current densities. Mass transport losses (overpotentials) which occur due to limited supply of reactant species to, and/or removal of products from the active sites are typically dominant at high current densities. No mass transport overpotentials were observed during the measurements. It was therefore, determined that the MFC was fully stabilized after 14 days of inoculation with acetate solution and ready for replacement with brewery wastewater for phase 2. The time dependent evolution of polarization curves in phase 1 was identical for operation with both CCMs.

Owing to the fact that the activation of the bio- and electro-catalyts had already been reached in phase 1, stabilization time was much

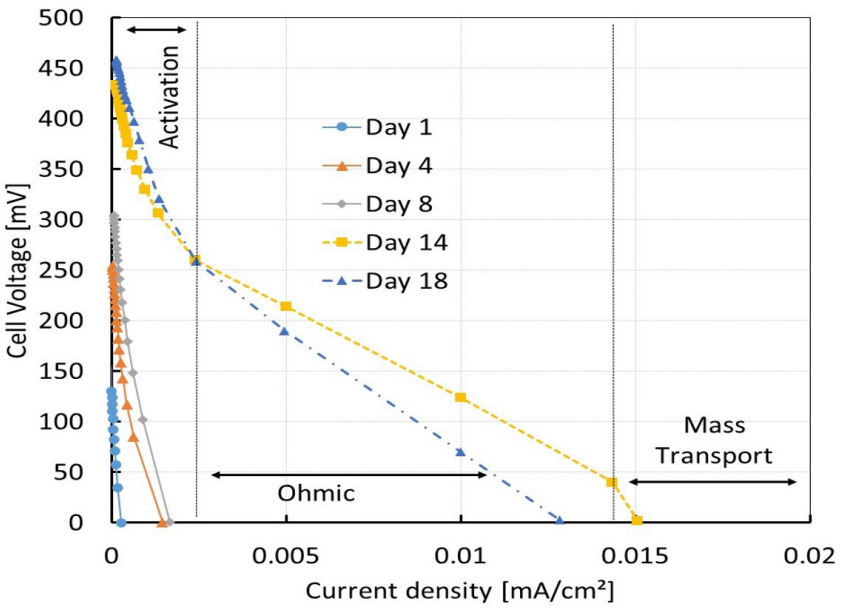

Fig. 4 Polarization with acetate solution (phase 1, using activated carbon CCM)

faster for phase 2, so stable and reproducible polarization curves were observed with both CCMs only after 5 days in phase 2. However, the MFC was operated for 14 days with brewery wastewater while monitoring the evolution of polarization curves daily.

Figure 5A-B shows the reproducibility of the polarization measurements in phase 2, while figure 5C shows the cell polarization on day 14 for both CCMs. The polarization curves reveal quite comparable performance for both CCMs. At the low current density region (< 2 µA/cm²) where the activity of the ORR catalysts is dominant, both the platinum and activated carbon CCMs showed the same performance, achieving a maximum open cell voltage of 350 mV. As expected, the thermodynamic voltages were ~ 19 % lower than those measured in phase 1, using the sodium acetate solution. The reason for the decrease in the thermodynamic voltage is the lower initial COD content in the brewery wastewater compared to the sodium acetate solution (Table 1). At high current densities (> 2 µA/cm²), the onset of ohmic losses could be seen with the activated carbon CCM. The better performance of the platinum CCM in the ohmic region is due to high electrical conductivity of platinum (~ 1.8 x10^7 S/m), which is about 7 orders of magnitude bigger than that of activated carbon. The ohmic advantage of the platinum catalyst is however not very significant to the overall comparative performance as can be seen in figure 5D where the power densities generated by both CCMs are compared. The power density curves show, that the performances of both ORR catalysts are very comparable throughout the whole range of external resistance. The maximum power densities achieved with the Platinum coated and activated carbon coated membranes were 0.49 mW/cm² and 0.45 mW/cm², both occurring at the same external resistance of 1.8 kΩ. At the maximum power densities, the cell voltage was 245.3 mV for the platinum and 238.61 mV for the activated carbon CCM.

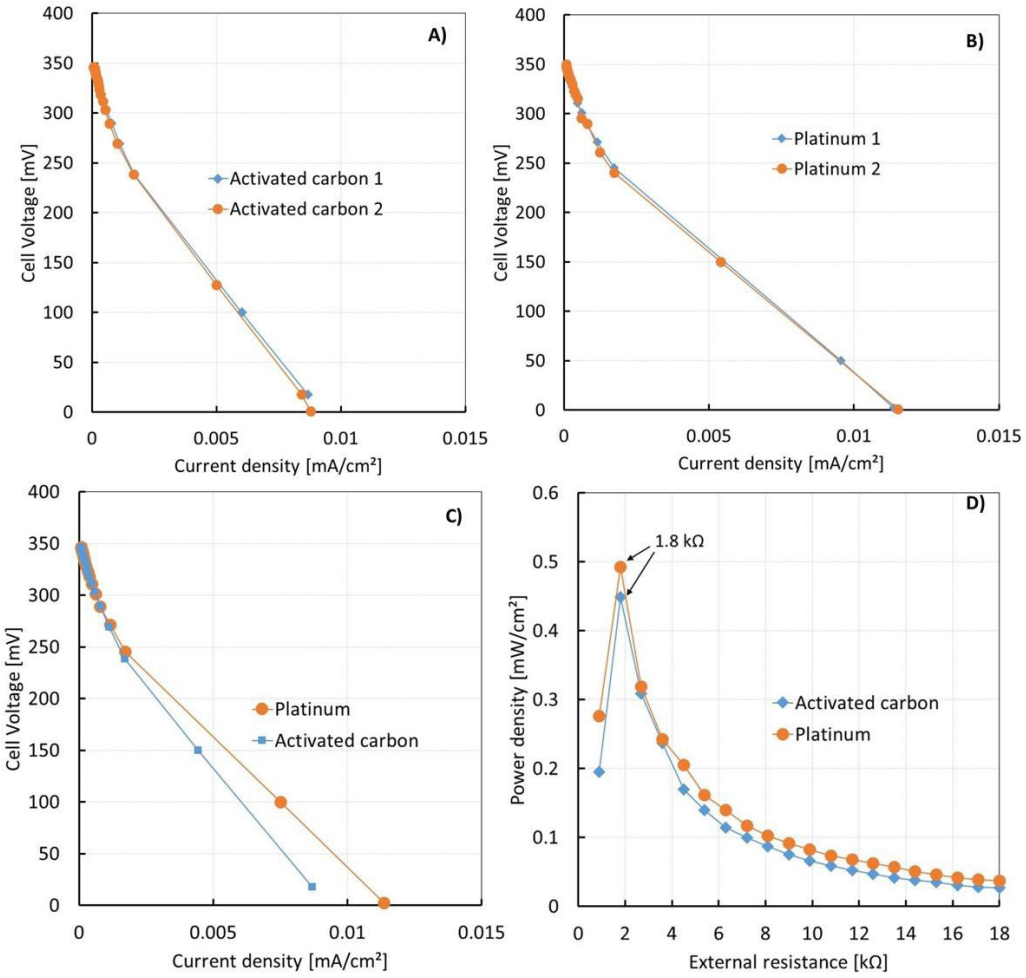

Fig. 5 **A) and B) showing the reproducibility of polarization curves for activated carbon and platinum respectively recorded on day 14 of phase 2 C) Direct comparison of the polarization of both CCMs recorded on day 14 of phase 2 D) Power density vs. external resistance of both CCMs operating with brewery wastewater as fuel source**

3.3 Stress test and coulombic efficiencies

Stress tests were performed on each CCM by letting the cell run for 14 days at optimal capacity (1.8 kΩ), on brewery wastewater (phase 3) while recording the

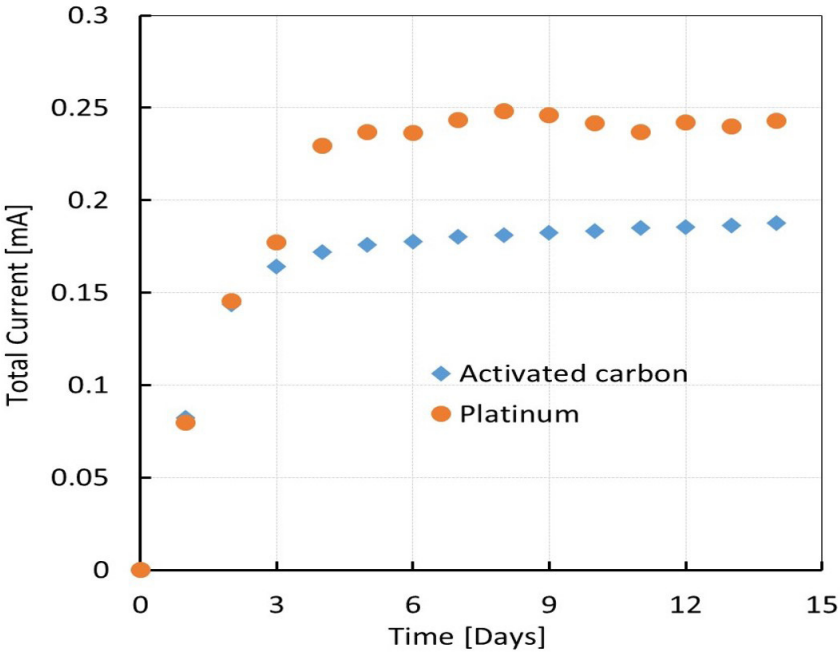

Fig. 6 **Stress test. Time dependent evolution of DC current at 1.8 kΩ external resistance**

evolution of electric current (Fig. 6). During this phase, polarization curves were not measured but electrolyte samples were collected once every day for monitoring. During the measurements, the temperature, pH and electrolyte conductivity remained relatively constant, so there was no concern about changes in physico-chemical properties affecting the overall cell performance.

Within the first two days of stress testing, both CCMs showed the same performance, with the generated electrical current rising sharply to 0.15 mA on day 2. The steep increase in performance continued with the platinum CCM on days 3 and 4, reaching 0.23 mA on day 4, while the activated carbon achieved 0.17 mA on day 4. After day 4, the performance of both CCMs plateaued during the next 10 days with the CCMs averaging 0.25 mA and 0.18 mA for the platinum and activated carbon respectively. The results from the stress test helps to expose and visualize the better activity of the platinum over the activated carbon CCM that could not be immediately visible from the polarization curves. The difference in higher catalytic activity of platinum over activated carbon does not lead to much improved performance because MFC operates generally at low current densities. In high current density applications such as PEMFC and AFC, the higher catalytic activity of Pt, due to its inherent properties, is often matched by a corresponding high cell performance improvement [30, 31].

To give a quantitative understanding of the difference in the performance of both CCMs, we calculated the coulombic efficiencies (according to Eq. 2) based on the COD removal and the electrical current generated during the stable region of the stress test. The platinum-coated CCM achieved a maximum coulombic efficiency of 14.5 %, while the maximum coulombic efficiency reached by the activated carbon coated CCM was 11.6 %. Both coulombic efficiencies fit well within the range of values that have thus far been reported in the literature [32].

4 Conclusions

We have compared the performances of activated carbon and platinum as ORR catalysts in MFCs by in-situ measurements. The performance characterization was based on COD removal efficiencies, cell polarization and coulombic efficiencies calculated under stress conditions. The maximum coulombic efficiencies were 14.5 % and 11.6 % for the platinum and activated carbon coated membranes respectively. The results show that, activated carbon can replace platinum as ORR catalyst for low current density MFCs without significant loss of electrical performance. This can be useful as cost saving solution, for large-scale and commercial MFCs, especially when the primary focus is on the biological treatment of wastewater.

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