Fall 11-13-2017

Microbial desalination cells with efficient platinum group metal-free cathode catalysts

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Recommended Citation

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This thesis is approved, and is acceptable in quality and form for publication:

Approved by thesis committee:

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Thesis

Submitted in partial Fulfillment oft he

Requirements for the Degree of

Master of Science

Chemical Engineering

The University of New Mexico

Albuquerque, New Mexico

December 2017

Acknowledgments

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Abstract

Iron-nitrogen-carbon based catalyst was used at the cathode of a microbial desalination cell (MDC) and compared with platinum (Pt) and activated carbon (AC) cathode. Fe-N-C catalyst was prepared using nicarbazin (NCB) as organic precursor by sacrificial support method (SSM). Rotating ring disk electrode (RRDE) experiments shows that Fe-NCB had higher electrocatalytic activity compared to AC

and Pt. The utilization of Fe-NCB into the cathode improved substantially the performance output with initial maximum power density of 49 ± 2 μWcm^{-2} in contrast to Pt and AC catalysts which have shown lower values of 34 ± 1 μWcm^{-2} and 23.5 ± 1.5 μWcm^{-2}, respectively. After four cycles, Fe-NCB catalyst lost 15% of its initial performance but still was 1.3 and 1.8 times more active than Pt and AC, respectively. Solution conductivity (SC) inside the desalination chamber (DC) decreased by 46-55% with every cycle. The pH of the cathodic chamber (CC) and the DC increased up to 10-11 due to the production of OH^- during the oxygen reduction reaction and the migration of OH^- into the desalination chamber. Chemical organic demand (COD) decreased by 73-83% during each cycle. It was shown that Fe-NCB and Pt had a similar coulombic efficiency (CE) of $39\pm7\%$ and $38\pm2\%$, while AC had lower CE ($24\pm5\%$).

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Chapter1. Introduction

Luigi Galvani, physician and professor at the University of Bologna, is considered the first electrochemist and bioelectricity pioneer. [67] In fact, with his experiments in 1780, he discovered that a dead frog leg's muscles twitched when struck by an electrical spark and coined the term "animal electricity" to describe the force that re-activated the muscles of this specimen as being generated by an electrical fluid that is carried to the muscles by the nerves. Alessandro Volta, a contemporary professor of experimental physics at the University of Pavia, checked Galvani's experiments and believed that the contractions occurred due to the metal cable Galvani used to connect nerves and muscles in his experiments. The Galvani-Volta controversy grew fervent at the end of the 18th century and was the platform that led shortly to the invention of an early battery, resulting from Volta's experiments. [68]

Significant advancements with electrochemical systems for power generation or energy storage have been made in several areas during the first few decades of the 19th century. It is important to cite, among the breakthroughs in electrochemical devices, the lead-acid battery that was invented in 1859 by the French physicist Gaston Plante, which is still playing a key role in the battery market, and the first H_2/O_2 acid fuel cell by William Grove. Grove is considered as the father of fuel cells: in fact, in a publication from 1838 on *The London and Edinburgh Philosophical Magazine* and *Journal of Science* he wrote about the development of his "gas

battery" [69] that inspired several scientists. Although in Electrochemistry: History and Theory, which was published in 1896, Wilhelm Ostwald described Grove's gas battery as "of no practical importance but quite significant for its theoretical interest", in 1889 Charles Langer and Ludwig Mond, coined the term "fuel cell" as they were trying to engineer the first practical fuel cell using air and coal gas. In 1932, a century after Grove's experiments, Francis Bacon developed the first successful hydrogen-oxygen fuel cell with alkaline electrolyte and in 1959 demonstrated a practical 5 kW system [70]. Advancements in fuel cells (FCs) were achieved in the following years, and accelerated with the involvement of NASA as well as national agencies and vehicle manufacturers.

Based on the fact that there is a shortage of available sources of clean water all around the world and this is becoming a global crisis in the near future, applying cutting edge technologies, including microbial fuel cells, to produce clean water from the extensive sources of high salinity water available in the oceans is of great importance. Different electrochemical based desalination methods have been introduced, of which, we can name electro dialysis which is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of a direct current (DC) voltage. The process uses a driving force to transfer ionic species from the source water through cathode (positively charged ions) and anode (negatively charged ions) to a concentrate wastewater stream,

creating a more dilute stream. ED selectively removes dissolved solids, based on their electrical charge, by transferring the brackish water ions through a semi permeable ion exchange membrane charged with an electrical potential. It points out that the feed water becomes separated into the following three types of water:

- Product water, which has an acceptably low conductivity and TDS level,
- brine, or concentrate, which is the water that receives the brackish water ions;
- electrode feed water, which is the water that passes directly over the electrodes that create the electrical potential.

EDR is a variation on the ED process, which uses electrode polarity reversal to automatically clean membrane surfaces. EDR works the same way as ED, except that the polarity of the DC power is reversed two to four times per hour. When the polarity is reversed, the source water dilute and concentrate compartments are also reversed and so are the chemical reactions at the electrodes. This polarity reversal helps prevent the formation of scale on the membranes. The setup is very similar to an ED system except for the presence of reversal valves. [158]

In this work, we are interested in BFCs since they operate under mild reaction conditions, namely ambient operational temperature and pressure, employ neutral or circumneutral electrolytes and use inexpensive catalysts and anodic fuel that can range from simple organic molecules like glucose or acetate to complex organic

waste, like waste waters and urine. BFCs could be defined as devices able to transform chemical to electrical energy via electrochemical reactions involving biochemical pathways and can be divided into enzymatic fuel cells (EFCs) [75,76,77] and MFCs. The former use selective enzymes to perform redox reactions that produce current while the latter utilize electroactive microbes to degrade organics and produce electricity. Generally, enzymes have better electrochemical catalytic performance but are unsustainable and less durable compared to microbes. The first report of an actual MFC dates back to the beginning of last century, when the English botanist Michael Cresse Potter demonstrated that microorganisms could generate a voltage and deliver current [78].

Biological fuel cells became popular in the 1960s, when NASA showed short-term interest in turning organic waste into electricity on space missions. Interest in BFCs was then reinvigorated in the 800 following Bennetto et al., who put emphasis on the MFC functionality with a focus on mediator-based electron transfer [79,80]. Since the beginning of the 21st century, interest in MFCs has been growing exponentially, as illustrated by the number of publications and related citations (Fig. 1).
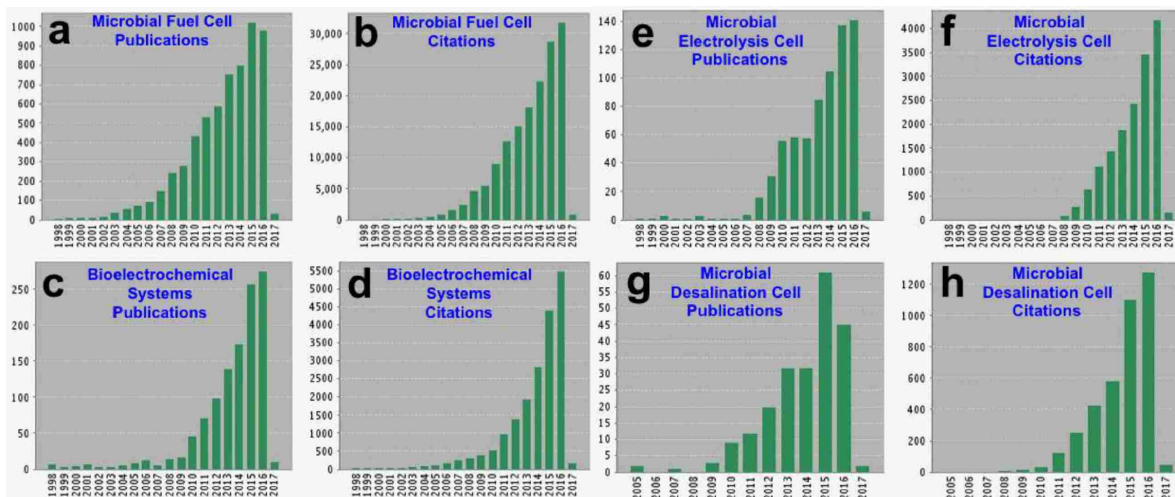
Fig 1. Quantitative analysis of the scientific literature on microbial fuel cells and bioelectrochemical systems (Source: ISI WEB OF SCIENCE, January 2017) [157]

BFCs convert the chemical energy of organics directly into electrical energy and use either a microorganism or an enzyme as the catalyst [81,82,83]. Enzymes possess remarkable advantages over chemical catalysts, such as biocompatibility, higher transformation efficiency, higher activity under mild conditions and particularly higher specific selectivity. The last two features enable the BFC to operate without a separation membrane, a factor that makes miniaturization possible and, in turn, the prospect of using enzymatic fuel cells in wearable and implantable devices, feasible [84,85,86]. Unfortunately, the enzymatic life time is short and it is even further shortened in the presence of pollutants [84,87,88]. The development of mediator-less enzyme-based bio-cathodes and bio-anodes has addressed one of the issues of EFC, i.e. the use of mediators. Also, the increase in the active lifetime of the immobilized enzymes through encapsulation in micellar polymers that avoid enzyme denaturation

and provide a biocompatible hydrophobic and pH-buffered environment contributed to the development of EFC [77,89,90,91].

The use of whole microbial cells in MFC for the bio-electrochemical oxidation of fuels is advantageous since it eliminates the need for enzyme isolation and still allows multiple enzymatic reactions to take place in conditions close to their natural environment, with the organisms regenerating the required enzymes as part of their natural life. On the other hand, they have a slower response time owing to the more complex chemical pathways. Although MFC target applications could span across scales, in general they differ from those for EFCs: MFCs can be typically envisaged for large-scale applications for wastewater treatment [192,93] or in small-scale for small and portable applications [94], EFCs are instead compact, miniaturized and flexible bio-electrochemical devices [77,95].

As mentioned before, MFCs are by far the most studied and reported BESs. The main motive for pursuing this technology is the potential for complementing the existing costly wastewater treatment systems with a technology that can actually be self-sustainable or even have a net positive energy output while pollutants are removed. A general schematic diagram of the microbial fuel cell is presented in Fig.2a. In parallel, several other bio-electrochemical systems of interest have been developed [96-100]. Among them, one of the most interesting and well investigated, is the Microbial Electrolysis Cell (MEC), which was firstly introduced in 2005 [101]. A

depiction of the microbial electrolysis cell is here presented (Fig. 2b). MEC requires an external source of electricity for electrolysis to produce hydrogen at the cathode, but this external energy supply is of a small amount, since most of the energy comes from the chemical energy extracted from substrates oxidized at the anode [102]. Consequently, hydrogen can be produced with a low consumption of energy utilizing bioelectrocatalysis supported by additional low energy power sources. MEC is of a particular interest since hydrogen is a precious gas produced and fundamentally needed for the upcoming hydrogen-energy economy [103,104]. Several developments and improvements concerning the increase in hydrogen production [105-108], improvements in cell design [109-111], removal of membrane [112-115], utilization of microbial catalysts [116-118] or Pt-free catalysts [119-127] have been successfully demonstrated. Recently a large-scale application has also been shown, dealing with the production of hydrogen from winery wastewater [128]. Recently, three examples have dealt with relatively large scale (order of magnitude of one liter and above) MECs [129-131]. This clearly indicated the intention of scientists to scale up the MEC systems towards practical applications, through studying the limitations related to the increase in reactor size. Most recently, other BESs have been developed with co-generative and trigenerative purposes. Among them, interestingly, microbial desalination cell (MDC) has been successfully developed with the tentative objective of treating wastewater, generating electricity and desalinating water simultaneously

[132]. A general schematic of the microbial desalination cell is here presented (Fig. 2c). Recent review works report on the main configurations adopted in microbial desalination cells [133-136], with the implementation of air-breathing [137-139] as well as bio-cathodes [140] and osmotic membranes [141] have been used. Also, other parameters were investigated for improving microbial desalination cells such as recirculating anolyte and catholyte [142], stacking the cells [143,144] and using capacitive materials for deionization [145-147]. A pilot MDC system of 105 L was also recently presented [148]. In parallel with this research activity, BESs have recently been presented as microbial electro-synthesis devices in which specific bacteria or operating conditions allowed the production of valuable products from CO2 or other compounds, including gas transformation or reduction. This relatively new direction is of high interest because of the possible utilization of renewable energy when disconnected from the main power lines distribution. The main principles of the microbial electro-synthesis cell are shown in Fig. 2 d.
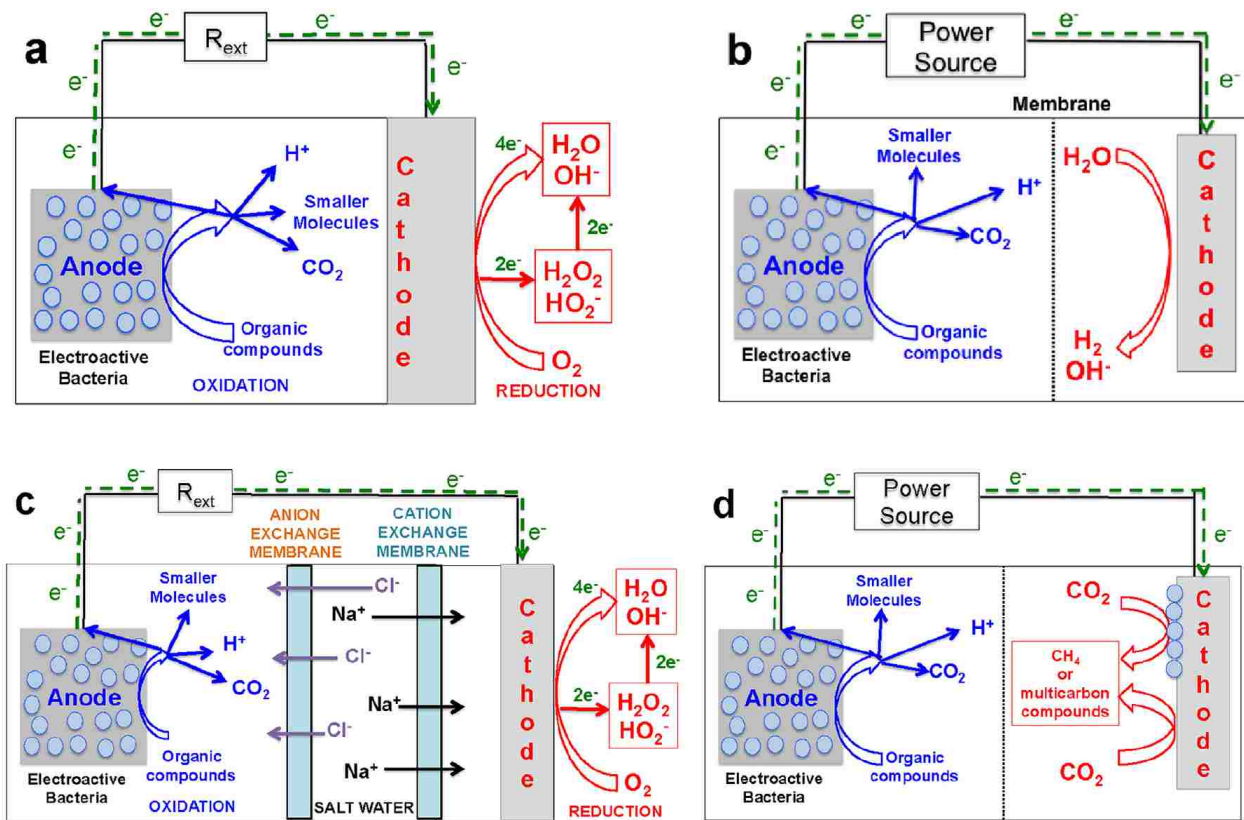
Fig 2. Schematic of a microbial Fuel Cell (a), microbial electrolysis cell (b), microbial Desalination Cell (c) and general Microbial electro-synthesis cell (d)

Interestingly, CO2 can be transformed to methane [149-151], acetate [149,150], formate [152] and other compounds [149,150,153-156]. While the feasibility of the process has been shown in several cases, numerous problems have still to be overcome. Among them, selectivity of the product, separation of the product from the solution, low reaction kinetics and cell design seem to be most challenging to address. Despite these difficulties, results are quite encouraging and deserve further investigations.

Nowadays, water availability is an important issue to seriously consider in our modern society. In fact, few of the several negative consequences of the climate changes are related to the variation of rain and snow patterns and reduction in rainy days with more concentrated events with much higher intensity. As a consequence, several places suffer from severe and prolonged draughts. Water quality is another problem that needs to be faced, especially in those countries worldwide with shortage of advanced wastewater treatment systems. [1-2] Roughly the 71% of the Earth surface is covered with water and looking more into details, over 97% of the overall water is in salty form stored into oceans. [1-4] Therefore, it seems rational to utilize this water for producing drinkable water by removing or separating the salts. Unfortunately, all the desalination technologies have high costs and are always associated with rich countries. This is due to high energy utilized or the employment of costly membranes. Distillation is the most utilized technology for desalinating seawater that operates exploiting the change in phase (from liquid to vapor) of the water due to increased temperature that is then condensed allowing the separation of water from the salts.[5-6] Another technology well known is the reverse osmosis that through the exploitation external pressure overcomes the natural osmotic pressure and separates the water from the salty water with the application of a selective semipermeable membrane. [7-8]

Recently, a novel bio-electrochemical system (BES) named microbial desalination cell (MDC) has been introduced with the tri-generative purpose of water desalination, electricity generation and wastewater treatment.[1] Differently than microbial fuel cells (MFCs), MDCs have a central compartment that is separated with two selective membranes (anion and cation exchange membrane) that allow to remove ions (mainly Na^+ and Cl^-) from the flow of salty water.[9-10] The electricity used in a MDC is due only to the pumping of the fluids within the three chambers and if that energy is harvested from the system itself, the MDC can work theoretically with no electricity input. Therefore, due to the low energy consumption, the MDC is considered a promising water desalination system.

Several aspects have been investigated into MDCs to increase desalination rate, boost the electricity generation and make a more robust system as recently presented in review papers.[11-12] Among those works, different configurations or operating modes were investigated for MDCs like the utilization of air cathode,[13-14] bio-cathode,[15] bipolar membranes,[16] capacitive features,[17-18] recirculation,[18-19] membrane stacking[20] were the aspects experimentally studied.[11-12] An important aspect for enhancing the MDC performances is the cathodic reaction. In the existing literature, potassium ferricyanide [9] and oxygen [21] have been used as oxidant at the cathode. The latter seems to be the most promising since it has high reduction potential and it is accessible at no cost and naturally available. Similarly, in MFCs,

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the oxygen reduction reaction (ORR) takes place at neutral pH conditions and it is severely limited by high overpotentials and low kinetic rate. [22-23] In fact, H^+ and OH^- are both essential reagents within the ORR and both are limited by definition to a concentration of $10^{-7}M$ in neutral pH hence lowering the kinetics. To enhance the reaction, the cathode is decorated with catalysts like platinum, [24-27] activated carbon [24-26,28] or platinum group metal-free (PGM-free) catalysts. [24-26] Platinum is quite expensive and for that reason not suitable for low energy producing devices in which containing the overall cost is imperative. Moreover, platinum is not the best candidate catalyst in polluted working conditions due to the binding of anions with the platinum sites. [10,24-27] AC is cheap, commercially available and durable in long-term operations but still performances remain low. PGM-free materials are based on M-N-C with M as earth abundant transition metals (e.g. Mn,[29-30] Fe,[31-37] Co[38-40] and Ni[41-42]) and they showed high stability and performances compared to Pt and AC.[43-45] Recently, Fe proved to have higher performances compared to Mn, Co and Ni in both rotating ring disk electrode (RRDE) and MFCs experiments .[46-47] Few examples of PGM-free catalysts used in MFCs in long terms operations are presented in literature with decrease in performances of 15-30% over one month operations.[43-45]

To the best of our knowledge, PGM-free catalysts were not investigated yet in MDCs. Here, we report the study of a new PGM-free catalyst with iron as

transitional metal and nicarbazin as organic precursor (Fe-NCB). This particular catalyst was not presented yet in any bio-electrochemical system. The kinetic of Fe-NCB was tested using rotating ring disk electrode (RRDE) in neutral media and compared with Pt and AC. Onset potential, half wave potential and limiting current were measured and discussed. Fe-NCB incorporated into an air-breathing cathode was tested firstly in clean conditions and then along four cycles in batch MDCs. The results were compared to Pt and AC used as baseline. Operating parameters like solution conductivity (SC), pH and COD removal were monitored along the experiments.

Chapter2. Materials and method

2.1. Catalyst preparation

Three cathode catalysts were utilized: the first one was Norit SX Plus activated carbon (AC) (Sigma Aldrich) also used as control material; the second one was platinum on carbon (10%wt) purchased from Alfa Aesar; the third one was iron-nicarbazin (Fe-NCB) that was in house made by Sacrificial Support Method (SSM) [62-64] in which monodispersed silica was used as support and wet-impregnated by mixing with solution of $Fe(NO_3)_3 \times 9H_2O$ (Sigma Aldrich) and Nicarbazin (Sigma Aldrich). The mixture was dispersed using mill-balls and then pyrolyzed at high temperature in controlled environment ($25°C$ min^{-1} ramp till $950°C$ then maintained for 30 minutes). The powder was then cooled down to room temperature and the silica was removed using HF (35-40%) exposing the powder to the acid in a contained plastic bottle overnight. The catalyst was then washed with water till circumneutral pH was reached and then dried at $80°C$ for at least 24 h.

2.2 Catalyst electrochemical measurements

Rotating ring disk electrode (RRDE) technique was used to measure the electrocatalytic activity of the three catalysts of interest (AC, Pt and Fe-NCB) in neutral media. An ink containing the catalyst was fabricated mixing 5 mg of the catalyst with 1 mL of liquid solution containing 85% in volume of isopropanol to water (ratio 1:1) and 15% in volume of 0.5%wt of Nafion solution. The sample was then ultra-sonicated for three minutes to disperse uniformly the catalyst within the solution. A pipette was used to drop cast the catalyst solution on the disk (area of 0.2475 cm^2) and afterwards the necessary time for the ink to dry was waited. Two potentiostats were used to measure the electrochemical performances of the catalyst; with one potentiostat, the disk current was measured instead with the second one the ring current was recorded. Particularly, the disk was the working electrode, a Ag/AgCl 3M KCl was the reference electrode and a graphite rod was used as counter electrode. The linear sweep voltammetry was run between a potential of +0.5V and -0.7 V (vs Ag/AgCl) at scan rate of 5 mVs^{-1} and rotating speed of 1600 rpm. The electrolyte used during these tests, was 0.1 M potassium phosphate buffer (K-PB) at pH of 7.5. Before initiating the electrochemical tests, the electrolyte was purged with pure oxygen for at least 20 minutes.

2.3 Cathode Fabrication

The obtained catalysts were integrated into air-breathing cathodes. [65-66] Particularly, a mixture of AC, carbon black (CB, Alfa Aesar, USA) and PTFE (60wt% emulsion, Sigma-Aldrich) was made considering a ratio in weight of 70, 10 and 20 percent, respectively. The mixture was grinded and pressed using a hydraulic press for 5 minutes. The material pressed formed a pellet on a 316stainless-steel mesh (McMaster, USA) used as current collector. The loading of AC/CB/PTFE was 40 $mgcm^{-1}$. In the case of Pt and Fe-NCB, the catalyst was mixed in the AC/CB/PTFE and then pressed. Pt and Fe-NCB loading was 2 $mgcm^{-2}$.

2.4 Cathode performances in clean conditions

After the fabrication, the cathode was inserted into a plastic single chamber with the cathode catalyst exposed to the electrolyte and the stainless-steel mesh exposed to the atmosphere. The cathode geometric area exposed to the electrolyte was 7 cm^2. The chamber was filled with 0.1M potassium phosphate at pH of 7.5. The cathode was left over night in contact with the electrolyte solution to increase the surface wettability of the cathode and avoid adsorbed oxygen on the catalyst surface. Linear

sweep voltammetry was used to test the electrocatalytic activity of the different cathodes in a three-electrodes configuration. Particularly, the cathode was the working electrode, Ag/AgCl 3M KCl was the reference electrode and a titanium coiled wire acted as counter electrode. Home-made Lugging capillary was used to bring the reference close to the working electrode. Polarization curves were run from open circuit voltage (OCV) till -0.1 V (vs Ag/AgCl) at a scan rate of 0.2 mVs^{-1}.

2.5 Microbial Desalination Cell Configuration

Three chambers configuration was used in this study. Particularly, the chambers had an empty volume of 33 mL (anode), 11 mL (desalination) and 33 mL (cathode). The desalination chamber was inserted between anode and cathode chamber. Anode and desalination chambers were divided by a cation exchange membrane (CEM, CSO, 100 μm, AGC Engineering CO., LTD, Japan). Desalination and cathode chambers were separated by an anion exchange membrane (AEM, Fumapem FAA-3-50 50 μm, Fumatech GmbH, Germany). In the anode chamber, a previously well colonized and working carbon brush (3×3 cm diameter and height, Millirose, USA) was used as anode electrode. The anode was filled with a solution containing 50% in volume of 0.05 M potassium phosphate buffer (K-PBS) and activated sludge respectively. A

solution of NaOAc (3 gL^{-1}) was used as bacterial food. The desalination cell was filled with a solution containing 30 gL^{-1} NaCl. The cathode chamber was filled with 0.023 M K-PB. Anode and cathode were connected to an external resistance of 100 Ω.

2.6 Electrochemical Analysis

Voltage was recorded over the eight days experiments using data log system. The polarization curves were done at the beginning and repeated at the end of the experiments to check the stability in performances after 8 days. Particularly, the MDCs were left in open circuit voltage for at least 2 hours in order to allow the MDC voltage stabilization. Three electrodes configuration was used during the record of the polarization curves with the anode used as counter electrode, the cathode as working electrode and Ag/AgCl (3M KCl) inserted into the desalination chamber, as reference. Chronoamperometry at different voltages were done with a stability time of 5 minutes each point allowing to separately record potential profiles of anode and cathode using a Biologic SP-50 potentiostat. Polarization curves were recorded at identical operating conditions. SC and pH were measured over time using Orion Star A112 (Thermo-Scientific, USA) and Benchmeter PHB-600R (OMEGA, USA)

respectively. COD was measured using standard HACH vials (Colorado, USA). Coulombic efficiency was calculated as the following equation (eq. 1):

$$CE = \frac{\int_0^t I \times dt}{\Delta COD \times \left(\frac{4}{32}\right) \times v \times F} \qquad \text{(eq. 1)}$$

in which on the numerator the current is integrated in the investigated time. On denominator, ΔCOD is the variation of the COD during the operations, $\frac{4}{32}$ is the number of electrons exchanged for oxygen used, v is the anodic chamber volume (125 mL) and F is the Faraday constant ($96485 \frac{A \times sec}{mol}$).

Chapter3. Results and Discussion

3.1 Rotating ring disk measurements

Rotating ring disk electrode (RRDE) technique is used to determine the kinetics performance of a certain catalyst into a well-defined media. The ring current obtained allowed to measure the undesired intermediate (H_2O_2) obtained during the oxygen reduction reaction (ORR). The more peroxide is produced, the more the ORR tends to follow a 2e- transfer mechanism rather than the preferred 4e- mechanism.

The linear sweep voltammetry obtained using rotating ring disk electrode measurements in O_2 saturated electrolyte (0.1 K-PB at pH=7.5) demonstrates the oxygen reduction catalysis of the Fe-NCB, with comparison to the standard activated carbon (AC) and platinum (Pt) (Figure 3). Different loadings of the catalysts (0.1 mgcm^{-2} and 0.4 mgcm^{-2}) are used to verify the trend in performance which is independent of the catalyst loading. It is observed that regardless of the catalyst loading, Fe catalyst exhibits the best catalytic performance in terms of the most positive onset potential (~0.2 V vs Ag/AgCl) and half wave potential of ~0.054 V vs Ag/AgCl for higher catalyst loading, and of ~0.044 V vs Ag/AgCl for a lower catalyst loading (Figure 3.a). The Pt catalyst exhibits a lower performance with a half wave potential of ~ -0.070 V vs Ag/AgCl at higher loading (Figure 3.a). The performance of both Fe and Pt catalysts are observed to be much better than the commercial activated carbon (Figure 3.a). As expected the lower loading of catalysts exhibit lower limiting current density (Figure 3.a). Ring currents for the different catalysts at different loadings are also here presented (Figure 3.b).

The trend discussed on the linear sweep voltammetry is confirmed in the H_2O_2 production (Figure 3.c) and the number of electrons transferred in the catalytic reactions for these catalysts (Figure 3.d). In general, the most efficient catalysts undergo a 4-electron oxygen reduction process and the least amount of peroxide production. (which is generated by the 2-electron mechanism) Fe catalyst shows the

least amount of peroxide over the entire potential range (<10%). Pt catalyst shows peroxide in the range of 10-20% in the entire potential range. Both Fe-NCB and Pt catalysts tend towards the 4-electron transfer process (Figure 3.d). On the contrary, AC shows a very high peroxide production (Figure 3.c) and largely exhibits a 2-electron process (Figure 3.d).
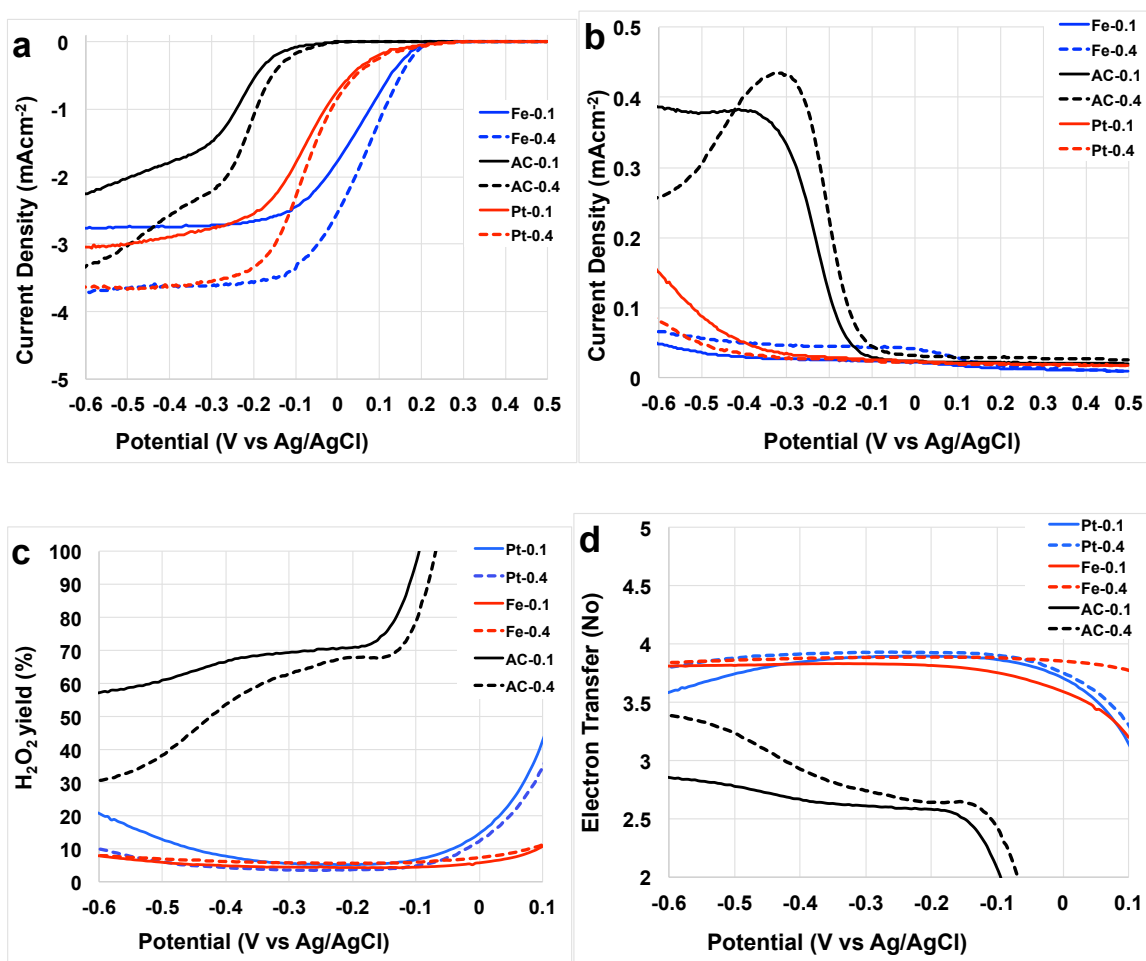

Figure 3. Disk current (a), ring current (b), peroxide yield (c) and electron transfer mechanism (d) of the three catalysts investigated at catalyst loading of 0.1 mgcm^{-2} and 0.4 mgcm^{-2}.

Those results are in agreement with previously reported data in which carbonaceous metal-free catalyst follow a 2e⁻ transfer mechanism, [48-50] instead PGM catalyst tends to follow a direct 4e⁻ transfer mechanism. Interestingly, PGM-free catalyst can follow a 2e⁻ or a 4e⁻ transfer mechanism, but, more generally tend to have a 2×2e⁻ transfer mechanism in which the intermediate (H_2O_2) is further reduced through another active site into the catalyst. The mechanisms involving the active sites function during ORR were recently presented. [51-52] Electro-catalytic analysis thus proves the superiority of Fe catalyst over Pt and the commercial AC. Pt is by far the best catalyst in acidic media but unfortunately, as the pH moves towards neutrality and even further to alkalinity, it loses its supremacy due to the negative interactions with anions within the solution that lower its intrinsic catalytic activity. Several studies have exploited this interaction with diverse anions. [44-46, 53-55] Despite Fe-NCB is mainly constituted by carbonaceous materials, the defects (iron and nitrogen) on the graphene sheet act as active sites that are able to lead to a direct 4e⁻ or a 2×2e⁻ transfer mechanism. A recent work, explain the possible transformations pathways of oxygen to the final product and the activity and responsibility of each active site towards each step of the reaction. [51-52]

3.2 Cathode Linear Sweep Voltammetry

After the tests done in RRDE, cathodes were fabricated and then tested in clean operating conditions using phosphate buffer electrolyte media. Linear sweep voltammetry of the fresh cathodes, after being left in contact with the electrolyte overnight, were then performed and the data are here reported (Figure 4).

Fe-NCB showed the highest open circuit potential (OCP) of 314±10 mV (vs Ag/AgCl) followed by Pt with 252±15 mV (vs Ag/AgCl) and AC with the lowest OCP (210±7 mV (vs Ag/AgCl)). During the LSV, Fe-NCB confirmed high electrocatalytic activity compared to both Pt and AC in agreement with the RRDE data.
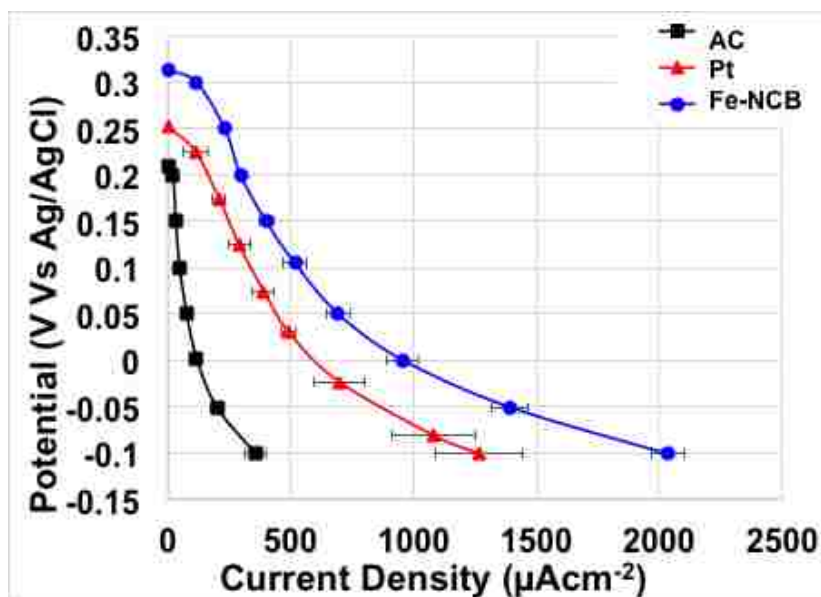
Figure 4. Linear sweep voltammetry of the cathodes in clean media

3.3 Voltage trend over 4 cycles

Microbial desalination cells with different cathode catalysts were tested during the course of four 2-day cycles. After every cycle, the solutions of each compartment were fully replenished and the MDCs were reconnected to the external resistance (R_{ext}) and voltage was recorded. Interestingly, the MDCs with Fe-NCB catalyst outperformed the MDCs operated with AC or Pt cathode catalysts during the four cycles (Figure 5).
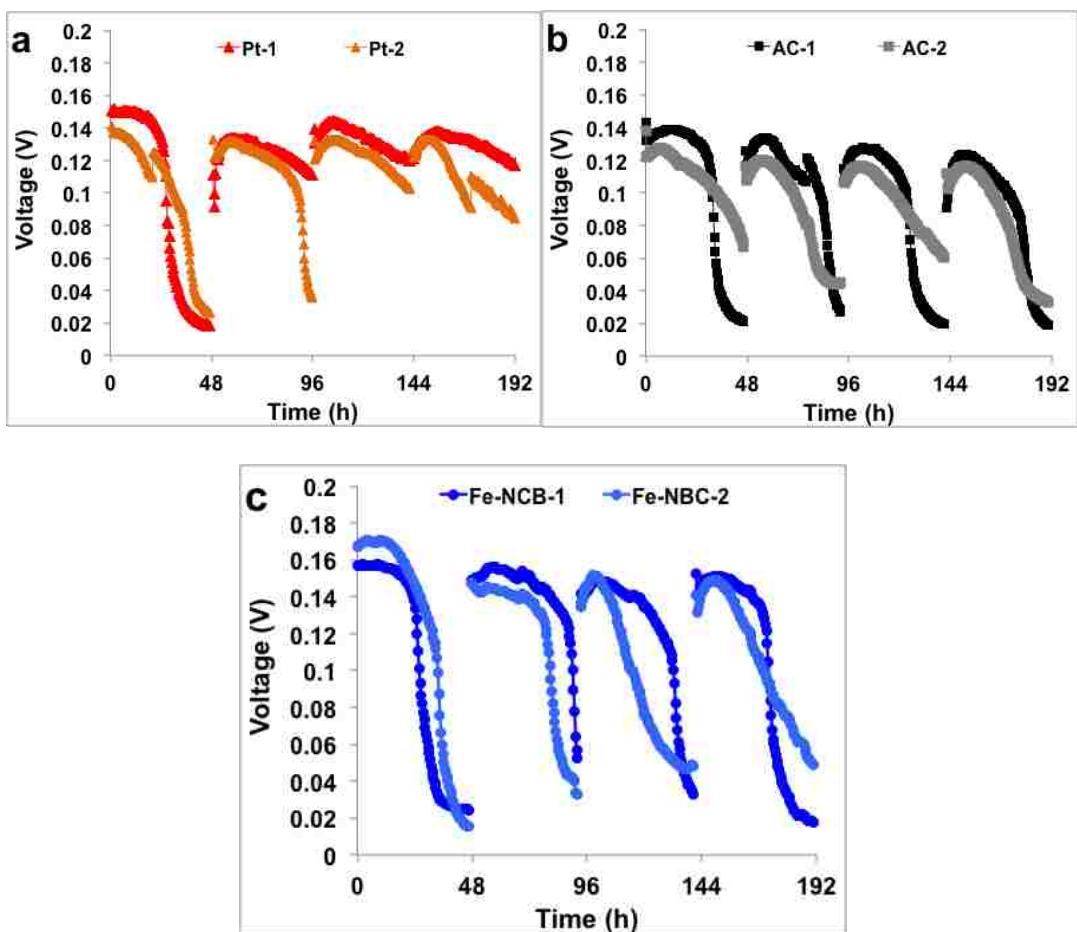
Figure 5. MDCs voltage trend over R_{ext} of 100 Ω for four cycles (192 hours) for Pt (a), AC (b) and Fe-NCB (c).

3.4 Polarization curves over time

Polarization curves of the MDCs with different cathode catalysts were examined initially and after the four cycles. Generally, the MDCs having Fe-NCB as catalysts had better polarization curves compared to Pt and AC cathode catalysts MDCs (Figure 6). Interestingly, initially, Pt and Fe-NCB had similar open circuit voltage

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(OCV) that was 60-70 mV higher compared to AC (Figure 6.a). After 4 cycles, Fe-NCB had an OCV of ≈640 mV (vs Ag/AgCl) that was 50 mV and 85 mV higher compared to Pt and AC respectively (Figure 6.b). Initially, MDCs with Fe-NCB had a maximum value of 49±3 μWcm^{-2} that was 1.5 times higher than Pt (32±3 μWcm^{-2}) and 2.2 times higher than AC (22±1 μWcm^{-2}) (Figure 6.c). After four cycles the maximum power recorded was 43±2 μWcm^{-2} for Fe-NCB, 34±1 μWcm^{-2} for Pt and 23.5±1.5 μWcm^{-2} for AC (Figure 6.d). After four cycles, the power measured slightly decreased of 15% for Fe-NCB, while it remains stable for Pt and AC. Fe-NCB had a power density 1.3 times higher than Pt and 1.8 times compared to AC indicating the superiority of iron based materials. The single electrode (anode and cathode) polarizations curves showed that both initially and after four cycles (Figure 7.a and 7.b), the anodes performed similarly and the main difference was given by the cathode behavior with Fe-NCB as the best performing material.

Only few detailed studies are presented on the durability of cathode catalysts in operating bio-electrochemical systems. The majority of those are long terms studied refers to roughly one month operations.[43-45, 47, 56] In those studies, the decrease in performances of AC or PGM-free catalysts was between 15% and 30% within the first month.[44-45] Moreover, it was shown that the degradation in activity of the Pt cathode was dramatic especially in the first few days or operations.[44-45] To the best of our knowledge, only two studies were done for a period of time longer than one

year[43, 56] and in those works, it was shown a decrease in performances of the cathode catalysts AC and Fe-based of roughly 25-30% that was more evident during the first month operations.[43, 56] The cause for the decrease in performances was attributed to the inorganic fouling as recently shown using x-ray micro CT tomography.[57-58]

3.5 Operating parameters variation along the cycles

SC was monitored for each compartment over time at the beginning and at the end of each cycle (Figure 8). Interestingly, the anode SC decreased from an average value of 7.43 ± 0.27 mScm^{-1} and terminated at 5.44 ± 0.29 mScm^{-1} (Figure 8.a). The final value was similar to all the MDCs. The decrease might be due to the consumption of acetate ions used as food by the electroactive bacteria on the anode electrode. The abundance of Na$^+$ (sodium acetate was used as bacterial feeding) within the anode chamber might also be the cause for slowing down the sodium ions transport from the desalination chamber to the anodic chamber because of the conservation of the electro-neutrality of the solution. SC decreased significantly into the DC (Figure 8.b) with initial average value of 48.05 ± 0.35 mScm^{-1}.

The average final SC value was 21.62 ± 0.92 mScm^{-1} for MDCs with Fe-NCB cathode catalyst, slightly higher SC for AC cathode MDCs with 23.21 ± 0.78 mScm^{-1} and for

Pt cathode MDCs with 25.90 ± 1.33 mScm^{-1}. After a two-day operation, the SC decreased by 55%, 52% and 46% for Fe-NCB, AC and Pt cathode respectively. Results did not underline a clear relationship between electricity output and desalination rate.
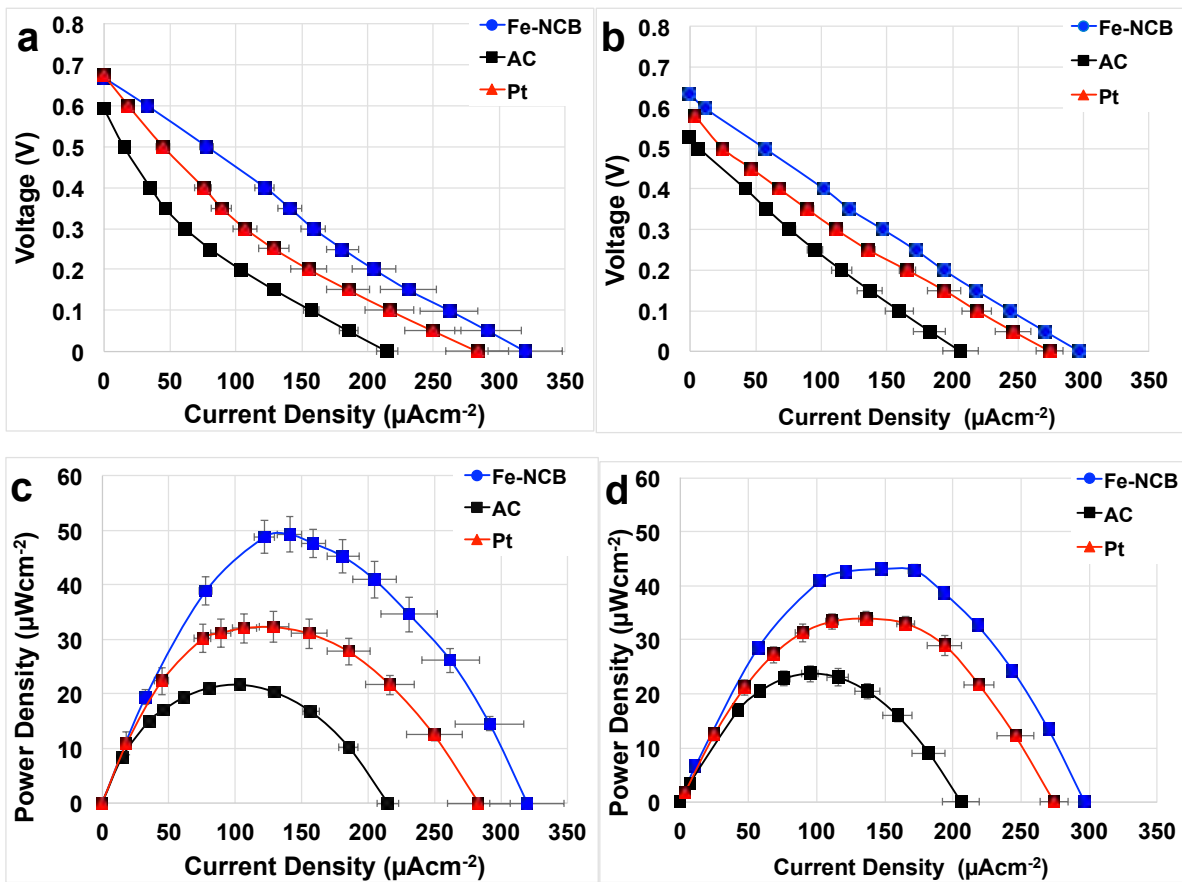
Figure 6. MDCs polarization curves initial (a) and after four cycles (b). Power curves initial (c) and after four cycles (d).
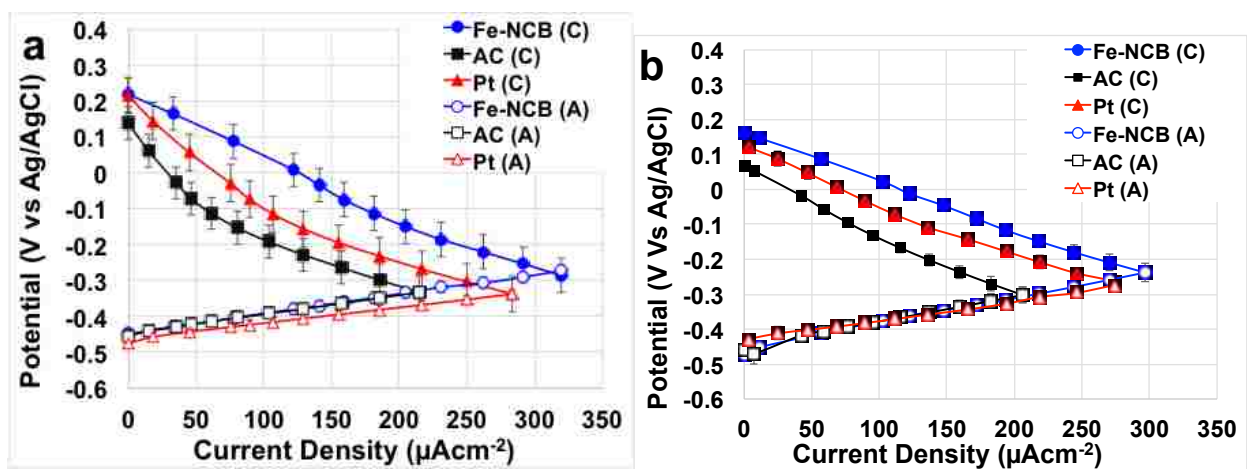

Figure 7. Anode and cathode polarization curves initial (e) and after four cycles (f).

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Consequently, we can speculate that other naturally occurring transport phenomena like forward osmosis and diffusion were predominant in the system. In fact, due to the low differences between the samples analyzed, it seems that in these operating conditions, the effect given by the MDC electrochemical performance is quite low. An increase in the volume inside the desalination chamber was detected but not quantified due to osmosis. At last, also cathode chamber SC was monitored (Figure 8.c) with values that triplicates the initial value stabilizing between 16.5 and 20.5 $mScm^{-1}$ independently from the catalysts utilized (Figure 8.b and 8.c).

Also, pHs were monitored over time (Figure 9). Initial pH in the anodic chamber was 7.85±0.17 that decreased in all the case to a lower value (6.5-7.1) probably due to the formation of H^+ caused by the oxidation reaction (Figure 9.a). Interestingly, both DC and CC pHs increased dramatically to value above 10. The DC started with a pH value between 6 and 6.6 and it increased their values between 10 and 10.7 (Figure 9.b). Even higher values were reached into the CC with pHs between 10.5 and 11.1 (Figure 9.c). The increase in the CC could be attributed to the production of OH^- of the ORR following the alkaline pathway. [10,59] It can also be speculated that the pH increase takes place initially in the cathode chamber and then the excess of OH^- moves to the desalination chamber crossing the anion exchange membrane for back diffusion transport phenomena. High pH might be beneficial for the PGM-free catalysts since it was shown before an increase in activity in alkaline

environment. [60-61] The increase in pH could also negatively affect the precipitation of carbonates compounds on the membranes, leading to lower the membrane ionic conductivity.

Figure 8. SC trend for anode chamber (a), desalination chamber (b) and cathode chamber (c) over the four cycles for the three different cathode catalysts investigated.

3.6 COD removal and coulombic efficiency

Organic compounds are used as fuel from the electroactive bacteria to function the oxidation reaction at the anode. Therefore, it is expected to see higher organics degradation when higher current/power is obtained. Organics removal was also measured through the variation of chemical organic demand (COD) over time. The average initial COD values in the MDCs were 1720 ± 350 mgL^{-1}. The COD degradation was in the range of 73-83%. Final COD values were 280 ± 187 mgL^{-1} for MDCs with Fe-NCB, 455 ± 289 mgL^{-1} for MDCs with Pt and 448 ± 199 mgL^{-1} for MDCs with AC. The COD consumption was 1720 ± 111 mgL^{-1}, 1557 ± 146 mgL^{-1}, 1250 ± 127 mgL^{-1} for Fe-NCB, Pt and AC respectively. This reflects that more organics are consumed when higher current/power is measured. The coulombic efficiency (CE) of Fe-NCB, Pt and AC was 39 ± 3%, 38 ± 2% and 24 ± 5% respectively.
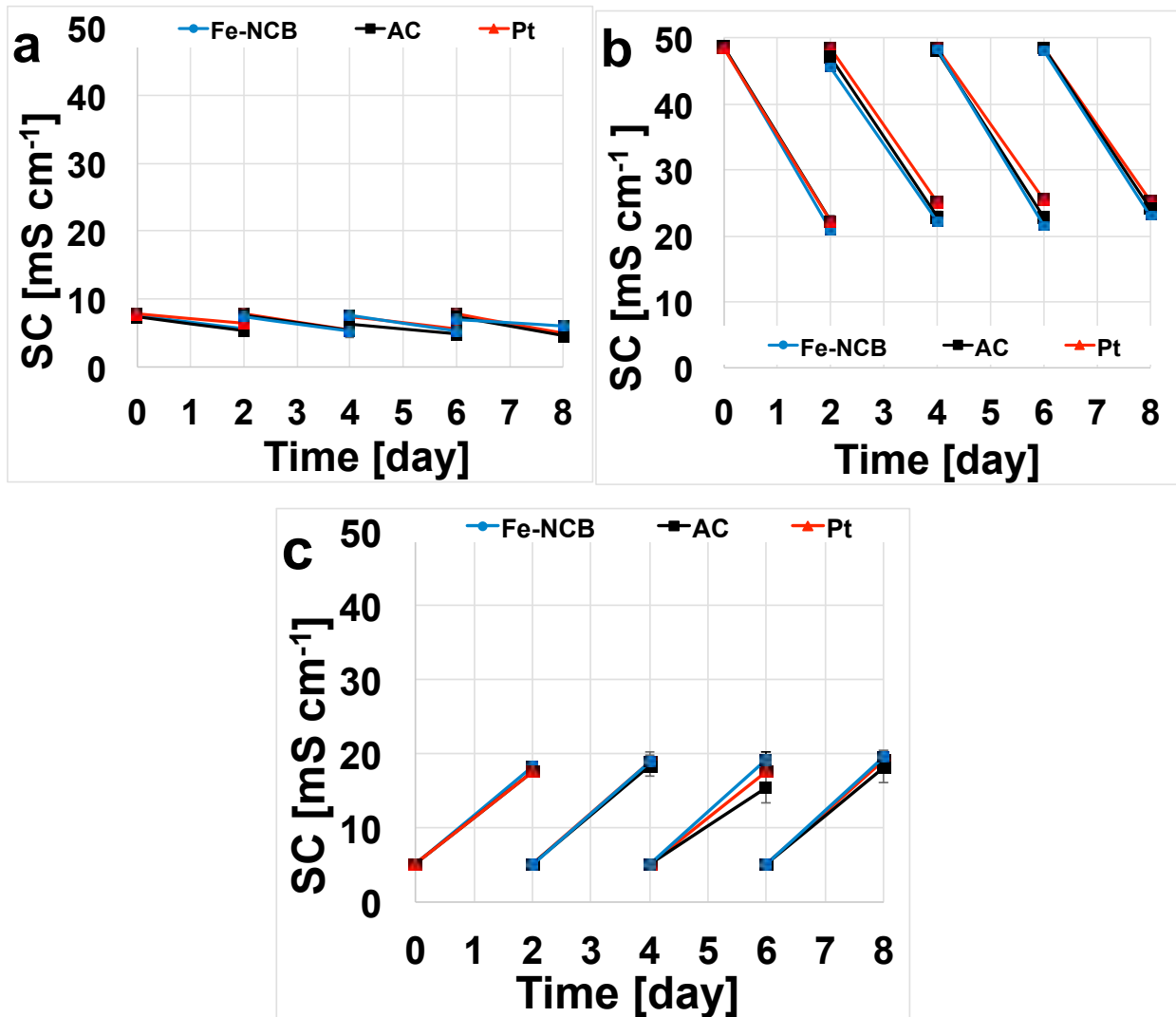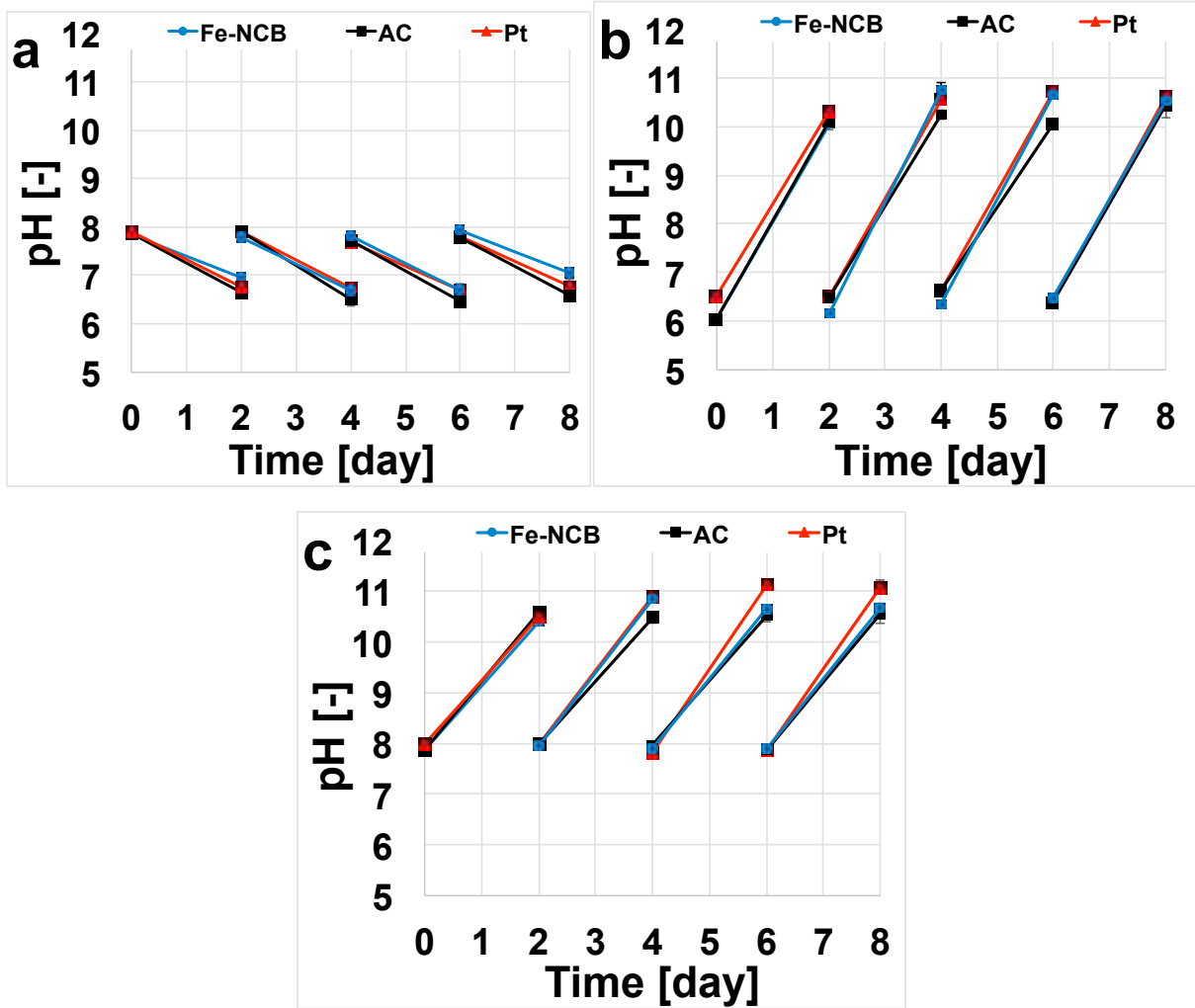
Figure 9. pH trend for the anode chamber (a), desalination chamber (b) and cathode chamber (c) over the four cycles for the three different cathode catalysts investigated.

Chapter4. Outlook and conclusions

For the first time, a PGM-free catalyst was used in an air-breathing cathode of a MDC. The ORR is often the limiting step of the red-ox reaction within bio-electrochemical systems and consequently a greater attention should be dedicated to enhancing this reaction. By far, literature has focused on utilization of potassium ferricyanide as oxidant and on Pt and AC as cathode catalysts. Potassium ferricyanide is not promising since it gives an additional cost to the system and it has to be replenished often. The ORR using Pt is not suitable for the high cost that makes the system not scalable and moreover, durability in polluted environments is quite questionable. AC has low performances for ORR in neutral media but seem instead to be a good support for metal-based catalysts. In this manuscript, the addition of a PGM-free cathode catalyst (Fe-NCB) boosts up the performances significantly. The performances remained 1.3 and 1.8-fold higher than AC and Pt over the time of the experiments. Fe-NCB cathode catalyst had the highest performances compared to AC and Pt and showed a good stability during the operations. High performances and low cost are the main characteristics of a catalyst material to be suitable for appropriate scale up and practical applications of bio-electrochemical systems. Moreover, due to the low applied loading (2 mg cm^{-2}), this cost does not engrave dramatically on the capital cost of the overall system. Interestingly, the higher

performances did not show an improvement on the desalination rate. In two days cycle, the SC in the desalination chamber was approximately halved. The pH increased in the cathodic and desalination chamber up to 10-11. The increase in pH into the cathodic chamber could also be used to enhance precipitation/recovery of nutrients or valuable added products (VAPs). Due to the low cost of iron, Fe-NCB is a promising alternative for Pt and very competitive material compared to AC.

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