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Advances in Air-cathodes and Ion-exchange Membranes for Microbial Desalination Cells

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Abstract

Microbial Desalination Cell (MDC) is a novel sustainable desalination technology. The main advantage of MDC is seen in the lower energy required to drive the desalination process (potentially 0.5 kWh m^{-3}) compared to conventional processes (up to 2-15 kWh m^{-3}). A typical MDC consists of a three-chamber reactor: an anode and a cathode chamber, similar to a conventional Microbial Fuel Cell, separated by a middle chamber containing saltwater. The desalination process is driven by the potential gradient produced between cathode and the anode. Anions (Cl^-) migrate to the anodic chamber and cations (Na^+) to the cathodic chamber through ion exchange membranes to maintain electroneutrality. Key components of MDC reactors are electrodes (anode and cathode), mainly based on carbon materials, and ion exchange membranes, based on ion-conducting polymers. MDC performance depends on materials characteristics and reactor configuration.
In our work, air-cathodes based on carbon nanofibers doped with metal nanoparticles (Fe and Co) were developed using the electrospinning technique as an alternative to costly catalysts (Pt). Moreover, anionic exchange membranes (AEM) with low electrical resistance, high permselectivity and anti (bio)fouling properties have been developed for maintaining desalination rates and achieve stable performance over time during MDC operation. After an extensive electrochemical characterization of the new cathodes and AEMs in three and four-electrode abiotic cells, air-cathode MDC reactors were constructed using the optimized components and tested in two scenarios: seawater (35 g_{NaCl}/L) and brackish-water (10 g_{NaCl}/L^1). Results indicate that air-cathode MDC is a suitable technology for desalinating both waters. However, this technology performs better in the brackish-water scenario, showing desalination rates up to 2.2 g_{NaCl}/m^2 h^1 with a salt removal percentage up to 60% after 72 hours of batch operation. In conclusion, air-cathode MDCs have shown to be suitable bioelectrochemical reactors to desalinate high conductivity water streams. Moreover, developed materials are promising for others bioelectrochemical systems.
Research leading to these results has received funding from EU-Horizon 2020 program. Grant Agreement Nº685793 (MIDES project).

Introduction

The world population continues increasing and it is projected that will increase in following years from (7.3 billion (2015) to 8.5 billion people before 2030) [1]. Water scarcity is one of the main global challenges to tackle in the coming decades due to this population increases in a context of climate change. Only 0.01% of total water is available on Earth surface as non-saline fresh water in our rivers, lakes, and streams; while saline water, from seas and oceans, represents about 97% of total water. There are two basic paths to minimize the water stress: reducing water consumption by population and reusing it. However, considering that about 2.4 billion people (about 40% of the world's population) live within 100 km of the coast and nearly 50% of all tourists travel to coastal areas [2], desalination water from oceans to produce usable water is a key option to significantly increase water resources for drinking, industrial and irrigation uses. In this context, there is a technological need to develop desalination technologies producing drinking water with low-energy demand. Global water desalination capacity is around 95 million m^3 day^{-1} [3]. Currently, there are different desalination technologies available in the market: Reverse Osmosis (RO) represents 69% of total desalination installations; Multi-stage flash (MSF) is 18% of plants; Multi-effect distillation is 7%, and Nanofiltration (NF) and Electrodialysis (ED) represent 3% and 2% of operational desalination plants. At present, desalination technologies require high-energy input to produce drinking water, for example RO consumes 3-6 kWh/m^3. This energy consumption is significantly higher than the one required for groundwater extraction (0.14-0.24 kWh/m^3) or the required for surface water treatment to produce potable quality water (0.36 kWh/m^3) [4]. In this context, MIDES project aims decreasing the energy demand of desalination process by developing a low-energy sustainable technology named Microbial Desalination Cell (MDC) as a pre-treatment for RO. The integration of MDC technology with commercial RO is sought to allow seawater desalination with an energy consumption below 0.5 kWh/m^3. MDC simultaneously treats wastewater and perform desalination using the energy contained in the wastewater. Wastewater contains up to 1.8 kWh/m^3 of chemical energy and MDC can harvest this and use it to drive the desalination process [4]. The MIDES process aims to take advantage of this energy to reduce the salt content of seawater or brackish water up to 5 g/L without the need of an external energy input. Then, the resulting water, with salinity of 5 g/L, is introduced to a RO to produce drinking water, requiring a total energy demand of only 0.5 kWh/m^3 [5] (Figure 1). Thus, the objective is to treat saline feedwater to reduce its salt concentration below 5 g/L.

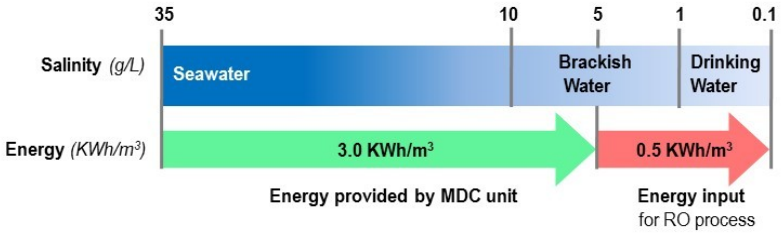

Figure 1. Energy concept for MDC coupled with RO.

The RO is a mature and widely used technology, thus, the challenge in MIDES project is to optimize the MDC reactor performance by overcoming current technological bottlenecks. The MDC is a bioelectrochemical system that was firstly described by Xiaoxin Cao *et al.* in 2009 [6] and different reactor configurations, materials for components, among others. have been reported for reaching an overall improvement of the MDC performance [4]. Mainly, MDC consists of a three chambers reactor: an anode and a cathode chambers, like a conventional Microbial Fuel Cell and a middle chamber containing saltwater separated by anionic and cationic exchange membranes (Figure 2). Organic matter is

oxidized by exoelectrogenic bacteria grown onto the anode, producing electrons. These are collected at the anode and transferred to the cathode by an external electric circuit. At the cathode, electron acceptor species, commonly oxygen, reacts with protons and electrons from the external circuit producing water. This reaction allows an electric current from the anode to the cathode, which is the main driving force for electric and ionic current. Also, the desalination process is driven by the potential gradient produced between the cathode and the anode. Anions (mainly Cl^-) migrate to the anodic chamber and cations (mainly Na^+) to the cathodic chamber through anion and cation exchange membranes (AEM and CEM, respectively) to maintain electroneutrality (Figure 2). Key components of MDC reactors are electrodes (anode and cathode), mainly based on carbon materials, and ion exchange membranes, based on ion-conducting polymers. MDC performance depends on materials characteristics and reactor configuration. In the present work, we firstly focused on the development, optimization and characterization of two of these key components: air-cathodes and AEM. After that, an air-cathode MDC was fabricated with developed components and its desalination performance was tested treating two types of feedwater (saline water, 35 g_{NaCl}/L, and brackish water, 10 g_{NaCl}/L).

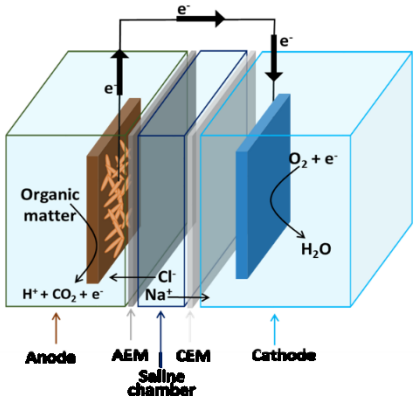

Figure 2. MDC scheme

1. Scientific Approach

The MDC is a complex reactor composed by four active components: two membranes (AEM and CEM) and two electrodes (anode and cathode). MDC reactor performance optimization must involve the improvement of each component and good compatibility between the components. The present work focuses on the development and optimization of AEM and cathodes (air-cathodes). Nevertheless, it is worth mentioning that in the framework of MIDES project also CEM and anodes have been optimized, as well as other reactor characteristics including reactor architecture, anionic, cationic and saline chamber volumes, electrode distances.

To develop AEM and air-cathode, this strategy has been followed: 1) know the key characteristics of the MDC components; 2) development of components; 3) material characterization and comparison with defined key characteristics; and 4) selection of best components and testing in MDC reactor.

The AEM membrane is placed between the anodic and saline chambers. Its role is to allow Cl^- (anions) migration from saline chamber to anodic chamber to preserve electroneutrality conditions due to anodic oxidation reaction. The key characteristics of AEM are the following: i) industrially production; ii) low electrical resistivity (RE, between 1-5 Ωcm^2); iii) high permselectivity (PS > 95%); iv) low ion selectivity; v) durability (operation at pH range 2-12); vi) low tendency for fouling (3-4 times less cleaning frequency comparing to current membranes); and vii) low cost manufacturing process (Roll-2-Roll coating). The optimization of AEMs has focused on developing a high antibiofouling membrane with proper ion and electrical conductivity properties. Different monomers have been coated

onto raw AEM membrane to increases the anti(bio)fouling effect. As counterpart, these coatings also increase the electrical resistance and decrease the permselectivity. Hence, a compromise is needed between the coating of monomers (to increase the antifouling) while maintaining electrical and ionic conductivity. In this regard, the electrical and ionic conductivity of AEMs have been assessed during the development phase, by studying their electrical resistivity and permselectivity.

In the case of air cathode, one of the main challenges is to develop air-cathodes with high catalytic activity of oxygen reduction reaction (ORR) performance, long term stability and low material cost (alternatives to platinum) [7]. Important properties to allow high ORR activity are materials with: i) high surface area (> 100 m^2/g), ii) suitable porosity (meso and micropores (pore diameter < 50 nm), iii) low electrical resistances (< 1 Ω cm), to avoid ohmic losses, iv) and high oxygen concentration at cathode surface, to avoid mass transport losses [8]. Carbon-based materials are suitable for air-cathodes because they can meet the abovementioned properties. Oxygen reduction from O_2 to H_2O in aqueous solution has slow kinetics due to the high activation energy required [9]. Consequently, the reaction must be catalyzed, and its kinetics highly depends on both the electrode and the catalyst materials. The ORR mechanism can be performed through a $4e^-$ or a $2e^-$ pathway, both occurring at the same time and in competition. The $4e^-$ pathway reaction is more convenient because it avoids the production of peroxide, which is corrosive, and can degrade the catalyst and MDC's membranes. Moreover, the $4e^-$ pathway can provide a higher open circuit cathode potential in MDC. Thus, to guarantee a proper ORR performance, the ORR should occur at potentials close to the formal potential and the difference between both is defined as overpotential [10]. For these reasons, air-cathodes electrodes based on carbon material and including different type of catalysts (MnO_2, Fe, graphene oxide (GO)) have been fabricated using techniques as electrospinning. Their ORR performances have been assessed using electrochemical techniques.

Finally, air-cathode MDC reactors have been constructed and operated using different membranes to evaluate their desalination performance. Also, the MDCs were operated and tested in two scenarios: seawater (35 g_{NaCl}/L^1) and brackish-water (10 g_{NaCl}/L). these two feedwater types have been selected because they represent 61% and 21% of total desalinated water [3].

2. Experiments and procedures

Membranes fabrication: Commercial Type 1 and Type 10 membranes from Fujifilm have been selected [11] to develop a suitable AEM, while different monomers (A1, B1 and A1+B1) have been coated to improve their antibiofouling properties compared with base membrane. A new optimized membrane (Type 16) has been developed considering the results obtained with Type 1 and Type 10 membranes. Once membranes have been tested at laboratory-scale, their fabrication have been performed by roll to roll production to evaluate industrial feasibility

Membranes characterization: The electric resistivity of AEMs was determined in a six-compartment electrodialysis cell (Figure 3, left). This cell was composed by two electrolytic chambers (n. 1, 6), two auxiliary chambers (n. 2, 5) and two chambers for membrane testing (n. 3, 4). The different chambers were separated by five membranes (3 CEMs, 1 AEM and the membrane tested). Before each test, the membrane under investigation was conditioned in the salt solution for 24 hours (NaCl 0.5M). The electrochemical cell was connected using an anode (ruthenium) as working electrode (WE) and a cathode (stainless steel) as counter electrode (CE) by a potentiostat. The electrochemical technique used was a chronopotentiometry, applying different constant current values between the electrodes and measuring the voltage drop generated across the membrane with two reference electrodes (Ag/AgCl), inserted into lugging capillaries and connected to the potentiostat. The slope of resulting current-voltage curve was equal to the electrical

resistance of the membrane. The resistivity was calculated by multiplying the resistance by the membrane surface.
On the other hand, membrane permselectivity was measured using a two chambers cell (Figure 3, right). The membrane was placed in the middle of the cell to separate the different chambers. In this case, the membrane was immersed in the same solution, with unequal concentration (0.1 and 0.5 M NaCl). After 30 minutes, due to the ion migration across the membrane, a voltage drop was generated and measured by two Ag/AgCl reference electrodes, with a multimeter.

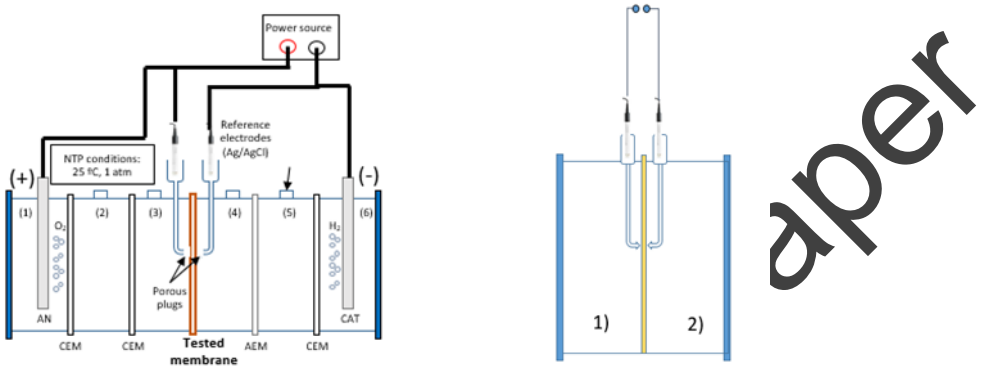

Figure 3. Electrical resistivity cell (left), Permselectivity cell (right)

Air cathodes fabrication: Air-cathodes electrodes are carbon nanofibers doped with catalysts (Fe, or graphene oxide (GO)) and have been fabricated by electrospinning technique: The electrospinning solutions were based on a mixture of PAN (9 wt%) and PVP (3 wt%) in DMF. The different developed cathodes were prepared by adding the catalyst precursor (Fe salts) or catalyst (GO) in the polymeric solution before the electrospinning process, homogenizing the mixture and finally fabricating the electrospun nanofibers. A post-treatment based on thermal treatment (Carbolite furnace) was done in a multistage process: 1) heating at up to 280 ºC, 2) dwelling time of 1 h at 280ºC under air and 3) heating step at up to 1000 ºC with a dwelling time of 1 h under N_2. (Figure 4) [10]. Moreover, SGL Carbon has fabricated prototypes of gas diffusion electrodes (GDEs) based on carbon paper coated with electroactive layers (carbon black, PTFE and high surface area MnO_2 catalyst).

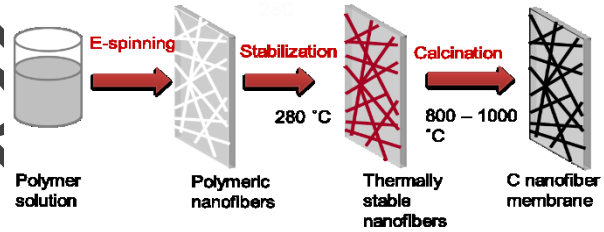

Figure 4. Metal doped carbon nanofiber fabrication process through electrospinning.

Air-cathodes characterization: The ORR performances of air-cathodes have been carried out with potentiostat/galvanostat. The abiotic electrochemical cell (Figure 5) is a three-electrode cell with a working volume of 40 mL. The electrolyte is 100 mM phosphate buffer (PBS) at neutral pH. The WE is a 6 mm disk (0.28 cm^2) of metal doped CNFs sandwiched inside stainless steel mesh; the CE is a platinum wire A-002234 and the reference electrode (REF) is Ag/AgCl electrode. Cyclic voltammetry (CV) has been performed with a scan rate of 10 mV/s from 0.4 V to -0.6 V vs Ag/AgCl starting from open circuit voltage (OCV) of WE. First, CV is performed after the bubbling of PBS with nitrogen for 30 minutes mixing at 500 rpm, maintaining the electrodes in open circuit voltage conditions and recording the open circuit potential (OCP) of WE. Once, the N_2-saturated CV has been carried out, the electrolyte is bubbled with oxygen for 10 minutes mixing at

500 rpm, maintaining the electrodes in OCV conditions and recording the OCP of WE. Then, the CV is performed with O_2-saturated PBS. After that, the sample is characterized with constant current method bubbling the sample with O_2 and with stirring. Two different constant current conditions are applied -0.5 mA/cm^2 and -1 mA/cm^2 for 20 minutes each one. Finally, constant voltage is applied bubbling the sample with O_2 and with stirring. Three different potential are applied +100 mV, -100 mV and -300 mV vs Ag/AgCl for 20 minutes each one.

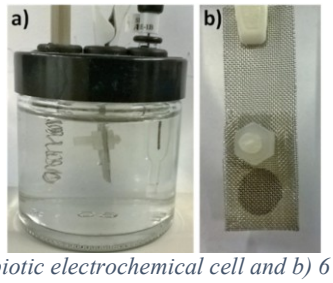

Figure 5. a) Three electrodes abiotic electrochemical cell and b) 6 mm circle metal doped carbon

Microbial Desalination Cell: A tailor-made air-cathode MDC reactors (Figure 6) are fabricated by LEITAT to test aforementioned materials. A flat plate MDC was designed and constructed in polycarbonate. The ratio among volumes of anodic-saline-cathodic solutions was 2.5:0.5:2.5 L, respectively. The surface area of electrodes and membranes in direct contact with liquid was 100 cm^2. The anode was made of carbon fiber fabrics from SGL Carbon inoculated with exoelectrogenic microorganisms. The cathode was made of iron doped carbon nanofibers, and the membrane was the Type10 membrane, from Fujifilm. MDC reactor was operated in batch mode with a batch time of 168 h, corresponding to a depletion of organic matter contained at anodic chamber (8 g of DQO). Recirculation of anolyte, catholyte and saline water was carried out by peristaltic pumps (5.7 L/h). During the desalination process, the MDC has been operated under external resistance of 2.5 ohms and it was connected to a potentiostat (SP-150, Biologic) to monitor electrochemical parameters over time. Reference electrodes (Ag/AgCl) were employed to monitor electrodes potentials. Air-cathode MDC have been assessed with two different types of feedwater: seawater (35 g/L) and brackish water (10 g/L).

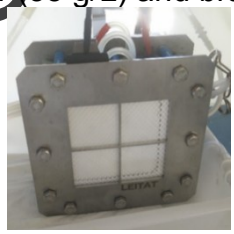

Figure 6. MDC reactor

3. Results

Membranes: Preliminary tests were dedicated to assessing membranes mechanical stability for MDC application with the designed reactor. Type 1 membrane was not robust enough, and has been replaced by Type 10 AEM, which had proper mechanical stability (avoiding pinholes). On the other hand, Type 10 membrane permselectivity decreased 30% approx. after 1000h of operation due to (bio)fouling. Different anti(bio)fouling monomers have been coated on Type 10 membrane to improve its performance (Type 10#2 and Type 10#16). These membranes have higher anti(bio)fouling properties lower electric and ionic conductivity respect to raw Type 10 membrane (Table 1). This could affect the desalination performance of MDC. However, in desalination experiment with air-cathode MDC (Figure 7), the performance of three membranes was similar, indicating that conductivity reduction was not critical for the MDC process. Type 10#2 and Type 10#16 have better anti(bio)fouling properties, thus these will have better stability along the

desalination operation time. A new and optimized membrane (Type 16) has been developed with lower electrical resistivity and higher permselectivity than Type 10#2 and Type 10#16 membranes (Table 1). Type 16 membrane also showed an increase in desalination rate compared to previous membranes (Figure 7).

Membrane	Resistance / Ω·cm^2	Permselectivity / %
Type 10	2.9	99.3
Type 10#2	5.0	72.7
Type 10#16	5.6	80.3
Type 16	2.4	96.5

Table 1. Electrical resistances and permselectivity of developed membranes and commercial membranes

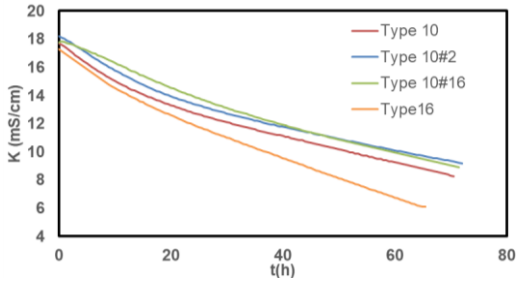

Figure 7. MDC desalination performance of membranes

Air-cathodes: the ORR performances of the following materials have been tested: i) carbon nanofibers doped with iron nanoparticles (*CNF-Fe*), ii) carbon nanofibers doped with graphene oxide (*CNF-GO*); and iii) gas diffusion electrode containing MnO_2 catalyst (*GDE-MnO$_2$*). CNF-Fe and CNF-GO have been fabricated by electrospinning technique being the catalyst incorporated in the polymeric mixture and after thermal treatment, this catalyst is present homogeneously in the carbon nanofibers. The presence of carbon nanofibers increases the surface area of electrode. *GDE-MnO$_2$* has been fabricated by coating a carbon paper with carbon particles and catalyst (MnO_2) bonded with PTFE. The performances of these materials have been compared with a commercial air-cathode based on carbon- manganese layer which is currently used in metal-air batteries and fuel cells (*AirCat*). cyclovoltammetries (CV) (Figure 8) show higher reductive current of AirCat material, while the CNF-Fe, CNF-GO and GDE-MnO_2 have lower reductive current. However, it is remarkable that AirCat sample has significant higher capacitance than the rest of materials probably due to its higher thickness and higher mass (Table 2).

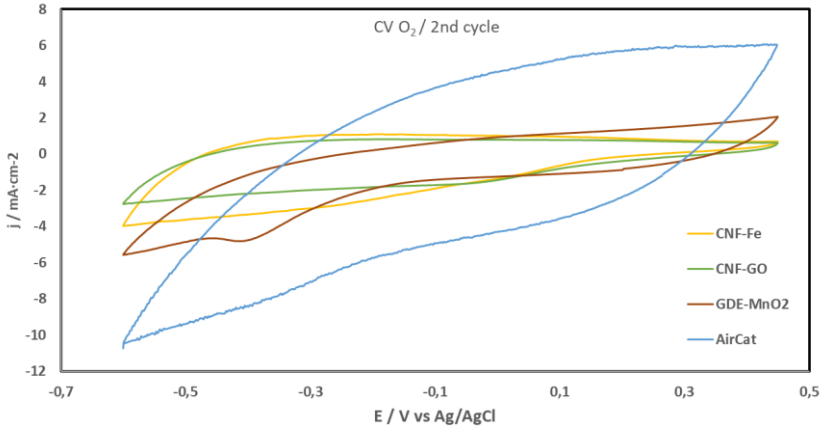

Figure 8. Cyclic voltammetry (CV) of material for air-cathode electrode.

Constant current (CstC and constant voltage (CstV) characterizations allowed evaluating the ORR performance of the materials in steady state condition. As Table 2 shows, under constant current of -0.5 mA/cm^2 and -1 mA/cm^2, the resulting potentials of materials are in the appropriate range (not high negative) and could allow good MDC performance. GDE-MnO_2 has higher overpotential than the rest of materials indicating a limited ORR

performance for the applied reductive currents. The constant voltage characterization shows similar current for AirCat, CNF-Fe and CNF-GO materials at applied voltage of +0.1 V and -0.1 V vs. Ag/AgCl. The higher reductive current of AirCat compared to CNF-Fe and CNF-GO determined in CV, for potentials between +0.1 and -0.1 V, is not observed at constant voltage technique because of the capacitance of AirCat material. GDE-MnO_2 shows lower current when potential close to overpotential is applied, but the current output at more negative potentials (-0.3 V vs. Ag/AgCl) is higher than other materials. Also, the current output of AirCat at more negative potentials is higher than CNF-Fe and CNF-GO materials. In conclusion, the ORR performance of four materials is in a suitable range for MDC operation. MIDES developed materials, based on CNF doped with Fe and GO, work properly at potentials close to overpotential which is important for MDC reactors.

		Constant Current		Constant Voltage		
	Mass	j = -0,5 mA/cm^2	j = -1 mA/cm^2	E = 0,1 V	E = -0,1 V	E = -0,3 V
MATERIALS	m / mg	E / V vs Ag/AgCl	E / V vs Ag/AgCl	J / mA/cm^2	J / mA/cm^2	J / mA/cm^2
AirCat	17.85	0.05	-0.03	-0.23	-1.63	-2.55
CNF-Fe	1.22	0.10	0.09	-0.43	-1.34	-1.78
CNF-GO	0.84	0.10	-0.03	-0.46	-1.12	-1.43
GDE-MnO2	4.56	-0.09	-0.12	-0.11	-0.64	-2.87

Table 2. Mass of air-cathode materials and potential and density current output of constant current and constant voltage characterizations.

MDC performance: MDC reactor has been operated and tested with two types of saline streams as feeding (seawater, 35 g_{NaCl}/L, and brackish water, 10 g_{NaCl}/L). The objective was to asses its performance in terms of desalination rate, final salinity, energy produced, etc. using both types of feedwater because they account for 80% of water used in current desalination plants. Figure 9 shows the desalination process of the two feedwaters. The air-cathode MDC was able to desalinate both waters with desalination rates of 2.8 g_{NaCl}/m^2 h and 1.3 g_{NaCl}/m^2 h for saline water and brackish water, respectively. Working in batch conditions for 168 h, the final concentration of salt was 15 g_{NaCl}/L for saline water and 2 g_{NaCl}/L for brackish water, corresponding to salt removal of 57 % and 82 %, respectively. Although, the desalination rate with saline water is higher, the MDC is not able to decrease the salt concentration to less than 5 g_{NaCl}/L in 168h operating in batch mode. Meanwhile, using the MDC to desalinate brackish water the objective to decrease the salt concentration below 5 g_{NaCl}/L is accomplished. The objective of 5 g_{NaCl}/L is defined because it allows this as inlet for the RO process and achieving drinking water quality standards at low energy demand (Figure 1).

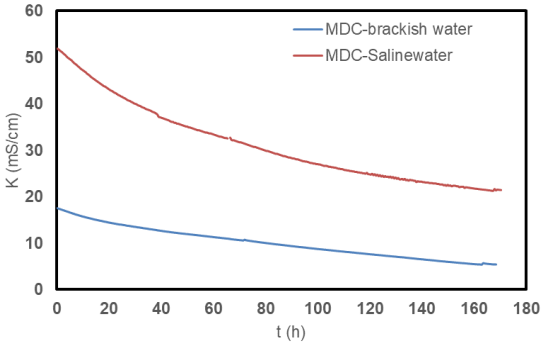

Figure 9. Desalination of saline (35 gNaCL/L) and brackish (35 gNaCL/L) water using an air-cathode MDC.

The desalination process is boosted by the electrochemical gradient between anode and cathode and the electrical charge as well as the charge circulating between electrodes. Tests in open circuit condition were performed for both waters to determine the desalination percentage due to diffusion as desalination also occurs due to this transport

phenomena. In this test, it was observed that desalination rates decreased significantly, being the salt removal rates less than 30%. Thus, the external circulation of electrons is mandatory to achieve high desalination performance and, moreover, these electrons can be harvested to produce electrically current. The MDC was operated under external resistance of 2.5 ohms, in order to operate the MDC close to short circuit conditions (not close to maximum power point). This operation allows high current densities and high charge (and ion) flow to achieve high desalination rates. In a desalination batch process (168h), the energy produced by the MDC accounts for 4 Wh/m^2 and 2.5 Wh/m^2 for seawater and brackish water respectively. Energy produced in experiments with seawater is higher because the current output is as well. This fact is due to the higher conductivity of saline chamber that decreases the MDC internal resistance, coherent with the higher desalination rate observed.

In conclusion, two key components of MDC reactor have been studied in the present work: i) air-cathodes based on carbon nanofibers doped with metal nanoparticles (Fe, GO and MOFS) were developed using the electrospinning technique, also gas diffusion electrodes were developed. ii) AEM with low electrical resistance, high permselectivity and anti (bio)fouling properties have been developed while allowing the same desalination rate withe stable performance over time during MDC operation. After an extensive electrochemical characterization of the new cathodes and AEMs, air-cathode MDC reactors were constructed with the optimized components and tested in two scenarios: seawater (35 g_{NaCl} L^{-1}) and brackish-water (10 g_{NaCl} L^{-1}). Results indicate that air-cathode MDC is a suitable technology for desalinating both waters. However, this technology performs better in the brackish-water scenario, showing desalination rates up to 1.3 g_{NaCl} m^{-2} h^{-1} with a salt removal percentage up to 80% after 168 hours of batch operation. Moreover, the MDC performs the desalination without energy demand to boost the process. On the contrary, it is able to harvest electrical energy. In conclusion, air-cathode MDCs have shown to be suitable BES reactors to desalinate saline streams. Finally, it is worth mentioning that herein developed materials are promising for being employed in others BES systems.

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