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Supercapacitive microbial desalination cells: New class of power generating devices for reduction of salinity content

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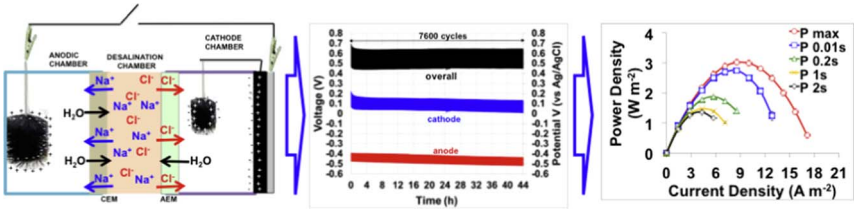
HIGHLIGHTS

- The concept of supercapacitive microbial desalination cell is here presented.
- The device is able to degrade organics, desalinate and generate power simultaneously.
- An additional electrode overcomes cathode ohmic losses and boost up power output.
- Maximum power achieved was 3.0 W m^{-2} (2.1 mW).
- 7600 discharge/self-recharge cycles were demonstrated over 44 h.

GRAPHICAL ABSTRACT

Supercapacitive Microbial Desalination Cell is here presented with unprecedented performances. Anode and cathode act as negative and positive electrode of an internal supercapacitor that is discharged and self-recharged. Maximum power of 3 W m^{-2} is recorded.



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ABSTRACT

In this work, the electrodes of a microbial desalination cell (MDC) are investigated as the positive and negative electrodes of an internal supercapacitor. The resulting system has been named a supercapacitive microbial desalination cell (SC-MDC). The electrodes are self-polarized by the red-ox reactions and therefore the anode acts as a negative electrode and the cathode as a positive electrode of the internal supercapacitor. In order to overcome cathodic losses, an additional capacitive electrode (AdE) was added and short-circuited with the SC-MDC cathode (SC-MDC-AdE). A total of 7600 discharge/self-recharge cycles (equivalent to 44 h of operation) of SC-MDC-AdE with a desalination chamber filled with an aqueous solution of 30 g L^{-1} NaCl are reported. The same reactor system was operated with real seawater collected from Pacific Ocean for 88 h (15,100 cycles). Maximum power generated was 1.63 ± 0.04 W m^{-2} for SC-MDC and 3.01 ± 0.01 W m^{-2} for SC-MDC-AdE. Solution conductivity in the desalination reactor decreased by ~50% after 23 h and by more than 60% after

Abbreviations: AC, activated carbon; AdE, additional electrode; AEM, anion exchange membrane; BES, bioelectrochemical system; C_{anode}, anode capacitance; CB, carbon black; $C_{cathode}$, cathode capacitance; C_{cell}, cell capacitance; CDI, capacitive deionization; Cell ESR, equivalent series resistance of the cell; CEM, cation exchange membrane; DC, desalination chamber; DI, deionized water; EDLC, electrochemical double layer capacitor; E_{pulse}, energy obtained by the pulse; Fe-AAPyr, iron aminoantypirine; GLV, galvanostatic discharges; i_{pulse}, , current pulses; KCl, potassium chloride; KPB, potassium phosphate buffer; MDC, membrane capacitive deionization; MDC, microbial desalination cell; MFC, microbial fuel cell; MFC, microbial fuel cell; NaCl, sodium chloride; NaOAc, sodium acetate; OCV, open circuit voltage; ORR, oxygen reduction reaction; PGM-free, platinum group metals-free; P_{max}, maximum power; P_{pulse}, power obtained by the pulse; PTFE, polytetrafluoroethylene; R_A, anodic anode ohmic resistance; R_C, cathodeic ohmic resistance; RO, reverse osmosis; SC-MDC-AdE, supercapacitive microbial desalination cell with additional electrode; SC-MDC, supercapacitive microbial desalination cell; SC-MFC, supercapacitive microbial fuel cell; SC, solution conductivity; SHE, standard hydrogen electrode; t_{pulse}, time of the pulse; t_{rest}, rest time; V^-, $_{oc}$, anode potentials in open circuit; V^+, $_{oc}$, cathode potential in open circuit; V_{max}, $_{OC}$, original maximum voltage in open circuit condition; V_{max}, practical voltage; $\Delta V_{capacitive}$, difference between V_{max} and V_{final} (at the end of t_{pulse}), voltage capacitive decrease drop; ΔV_{ohmic}, $_{cathode}$, cathode ohmic drop; ΔV_{ohmic}, difference between $V_{max,OC}$ and V_{max}, ohmic drop

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44 h. There was no observable change in the pH during cell operation. Power/current pulses were generated without an external power supply.

1. Introduction

The constant increase in living standards has increased utilization of natural resources, including a depletion of water resources and a dramatic decrease in the water quality in natural water sources. Water scarcity, water quality, and related sanitation issues are tremendous problems in poor and developing countries. High energy consumption is also important for water treatment. Nowadays, the majority of the energy utilized is derived from fossil fuels rather than from renewable sources. Water and energy related subjects are the two most problematic challenges that humans have to face and solve. Therefore, sustainable and alternative solutions need to be investigated.

The majority of the available water on Earth (over 96.5%) is salty water coming from the oceans that count for over 71% of the planet surface [1–5]. It seems natural to recover drinkable water from salty water. Several desalination technologies have been successfully explored over time. Despite high efficiency reached in desalinating, the main factors that limit the large-scale application worldwide seems to be the elevated cost and energy consumption [6–8]. The main existing technologies used are based on utilization of either heat (distillation) or membranes (reverse osmosis or electrodialysis). Presently, distillation produces roughly 60% of all drinking water obtained by desalination but the main problem of this technology is that the desalination plant has to be located in a proximity of a power plant and use its waste heat [9–12].

The second method is based on utilization of membranes, such as reverse osmosis [13–16] and nanofiltration [17–20] for large-scale desalination of water. These processes are driven by the application of an external pressure to overcome the natural osmotic pressure and forcibly push the water through the membrane. The main difference between reverse osmosis and nanofiltration is that the first one theoretically is able to eliminate all the ions while the second one primarily removes divalent ions. Thus, nanofiltration is not suitable for seawater desalination since that mainly consists of monovalent ions. Reverse osmosis is very expensive due to the membrane cost and the utilization of a large amount of energy. It is not surprising that reverse osmosis is mainly used in highly developed countries and in countries with large availability of inexpensive sources of energy derived from fossil fuels.

Another technology used is electrodialysis, in which positive and negative electrodes create an electric field that separates ions by migration towards opposite charged electrodes [21–24]. Under externally applied potentials, the anode is positively charged, cathode is negatively charged, and ion flux is controlled by anion exchange membranes facing the anode electrode (positively charged) and cation exchange membranes facing the cathode electrode (negatively charged). The charged electrodes attract counter-ions from the central flow through specific membranes. This method also requires a considerable amount of energy.

Capacitive deionization (CDI) is another promising technology under consideration [25–28]. It is based on utilization of high surface area carbon materials at two electrodes. A potential difference is applied to charge positive (anode) and negative (cathode) porous electrodes [25–28]. CDI is based on two consequent processes of adsorption and desorption in which ions are first separated from the salty water and therefore water is desalinated. In the adsorption process, electrical double layers (EDLs) are formed on both charged electrodes through the attraction of ions that are separated from the water. The solution between the electrodes is replaced and the electrodes are then discharged to null voltage, energy is delivered, and ions are released into the solution (which becomes a waste stream) [25–28]. A technology slightly different from CDI is achieved with the addition of membranes, known as membrane capacitive deionization (MCD) in which anion-selective membrane is inserted on the positive electrode and a cation exchange membrane is used on the negative electrode [29–33]. Compared to CDI, MDI is able to operate with lower energy consumption and better salt separation. However, the membranes significantly increase the overall costs of desalination system. In both cases, the discharges processes take place with a potential generated that is quite low (not greater than 200–300 mV) and consequently energy recovered cannot be used for any practical application.

New technologies for desalinating of salty water or reducing the salt content within a water stream have been recently introduced with promising results [34–38]. Particularly, microbial desalination cells (MDC) have captured the interest of the scientific community. The most studied bioelectrochemical systems (BES) are microbial fuel cells (MFC) [34], which are electrochemical devices in which electroactive bacteria are the anodic catalysts and able to oxidize pollutants and/or transform nutrients [39–44]. An MDC is a BES device derived from a microbial fuel cell in which anode and cathode compartments are further divided by ionic selective membranes (anion and cation exchange membrane) [35,45,46]. While current is generated due to the organic degradation at the anode and the oxygen reduction reaction (ORR) at the cathode, ions move through the exchange membranes, mainly due to osmosis and diffusion [47–51]. Interestingly, the open circuit voltage (OCV) is similar to the voltage in MFCs but total power and current generated are lower due to losses associated with addition of membranes [52]. The result is a tri-generative device that simultaneously treats wastewater by degrading organic pollutants, produces electricity, and decreases the salt content in the desalination chamber [47–50]. Several examples of MDCs have been shown in literature [53–63].

Several challenges have to be overcome for MDC technology to be viable; for example, the ion flux rates are low and the extent of desalination is significantly lower than existing desalination technologies. Another problem is related with the low power production from MDC that is 2–3 times lower than MFCs [47–49]. Moreover, electrode materials (anode and cathode) have to be tested in long term operations and costs have to be significantly reduced to be competitive with other desalination technologies [47–49]. Anode materials need to possess mechanical strength, resistance to bio-corrosion, and high electrical conductivity. Concerning the cathode materials, the cost has to be decreased and platinum cathode catalysts have to be replaced with more affordable and higher performing carbonaceous high surface area catalysts [34,47–50] or platinum group metals-free (PGM-free) catalysts [34,47–50]. In parallel, membrane costs have to be decreased with substantial increase in membrane durability. At the moment, membranes are a significant contributor to the cost of the entire MDC system. Membrane fouling and biofouling seem also to affect negatively the ion exchange rates over time and decrease the performance [47–49].

In this study, we combine the advantages of MDC and CDI within a novel system which we call a supercapacitive Microbial Desalination Cell (SC-MDC), presented here for the first time, in order to increase the power/current produced. The supercapacitive features of the MDC electrodes are used as an internal supercapacitor. The operation of SC-MDC in pulsed and intermittent modes over 44 h were reported. Power/current pulses are generated along with the decrease of salt content and organics. The electrochemical response of the SC-MDC is shown as well as solution conductivity and pH of the solutions monitored over time. An additional capacitive electrode (AdE) was used to overcome cathode ohmic losses and achieve higher power output. In order to decrease the