

RESEARCH PAPER

Cost-effective microbial water desalination cells

Eman A. Mahmoud^a, Eman O. Taha^a, Nevine O. Shaker^a, Usama F. Kandil^{a,*}, Mahmoud M. Reda Taha^b

^a Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

^b Department of Civil, Construction, and Environmental Engineering, University of New Mexico, Albuquerque, NM, USA

Abstract

This work aims to develop new microbial fuel cells (MFCs) by combining new electrode and selective membranes using biochemical reactions catalyzed by bacteria. The obtained results provide a simple methodology to develop and produce a new microbial desalination cell (MDC) by combining new polymerically modified electrode and selective ion-exchange membranes (cation and anion).

The process is a simple method for successful production of MDC in which the setting up of the MDC was performed by combining new polymerically modified electrode and selective membranes. To enhance the electrode conductivity to be suitable for electron transferring, carbon cloth material was treated with a conducting polymer. Poly (3,4-ethylenedioxythiophene) was used for this treatment. The growing of poly (3,4-ethylenedioxythiophene) nanostructures on carbon cloth substrates was performed through a facile one-step hydrothermal method. In combining with the anion-exchange membrane and cation-exchange membrane, this polymerically modified electrode was successfully used to produce MDC.

Finally, the water desalination process that was carried out proved that an electric current can be easily obtained through electrons that result from chemical reactions that take place due to the presence of bacteria, as this electrical energy is effectively useful in desalinating water.

Keywords: Bacterial growth, Hydrothermal polymerization, Microbial fuel cell, Water desalination

1. Introduction

Water is considered the most important element in human formation and survival, as water constitutes the basic component of the human body, and therefore no vital process in the human body is completed without water. In general, water is considered an essential element for life in general, as it is included in all human activities, starting with agriculture and industry, and other requirements that surround them. However, the challenge is the leakage of drinking water because about 97% of the water on Earth consists of saline water and most of the existing water is salty, which cannot be used directly for drinking purposes without further desalination process.¹

Therefore, providing drinking water on the surface of the Earth is considered one of the greatest challenges for human life because freshwater presents in a percentage that does not exceed two or three percent of water at most.² Therefore, scientists are making many research efforts in order to obtain drinking water by using several methods. Most of these methods depend on using energy, which is mostly provided by nonrenewable energy sources³ to desalinate seawater, and this is the reason for the inability to use this method in an applied manner due to its high cost due to the fuel needed to perform the desalination process. In addition, the required energy is of the type of nonrenewable sources that have a harmful impact on the environment. Besides, these desalination processes may

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* Corresponding author at: Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt.
E-mail address: alfa_olefins@yahoo.com (U.F. Kandil).



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also cause greenhouse gas emissions and climate change.^{4,5}

The process of desalinating water using conventional methods has a high cost due to the use of petroleum fuel in the treatment process. Therefore, it is important to find new effective methods for the water desalination process that are safe and have an acceptable cost. Research activity is currently turning to generating energy using a microbial desalination cell.³

Recent research activities have led to this type of cells, which is used to obtain electricity by decomposing organic compounds using types of micro-catalysts from living organisms.^{6–8} Therefore, these cells are a process of producing electricity using electrons generated from biological reactions catalyzed by bacteria.

In general, the idea of using this type of cell is that it has the ability to convert the electrons that result from the oxidation process of bacteria into reducing substances on the anodes and oxidizing substances on the cathodes, which results in an electric current in the external current circuit.⁹

The ion-exchange membranes (cations and anions) recently found a lot of research activities and have been prepared previously in simple and cost-effective methods.^{10,11} In this research, we successfully achieved energy generation through bacterial interactions using these membranes, and the produced energy was used in the desalination process.

In this work, we introduced a simple method for successful production of microbial desalination cells (MDC) in combining with new polymerically modified electrode and selective membranes. The process started with treating the carbon cloth (CC) material with poly (3,4-ethylenedioxythiophene) (PEDOT) as a conducting polymer. Then, MDC was fabricated with the modified electrode, anion-exchange membrane (AEM), and cation-exchange membrane (CEM). The produced MDC was fully characterized and successfully applied in a desalination process.

2. Experimental

2.1. Materials

The used carbon fiber composite is Toray Carbon Paper 030, Wet Proofed (30%), size (40 × 40 cm), which is a paper suitable for use as a catalyst backing layer. The carbon fiber fabric is chemically pure fabric with low oxidation rate. An aerobic activated sludge from a local municipal wastewater treatment plant (Gabal Al Asfer WWTP, Egypt) was

used for the biofilm growth. The type of the used cathode was gas diffusion CC electrode. Titanium wire, (0.25 mm diameter), 99.7% (metal basis), Thermo Scientific Chemicals, was used as the current collectors. All carbon materials, including carbon fiber cloth, are used as received. 3,4-ethylenedioxythiophene (EDOT) with a purity of 98% and pure ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) ACS reagent, 97%, were used as received. All reagents, including nitric acid, hydrochloric acid, and ethanol, were used as received.

2.2. Pretreatment of CC substrates

First, CC ($1.5 \times 1.5 \text{ cm}^2$) was dipped in concentrated nitric acid at 60 °C for overnight. The CC substrates were then thoroughly washed with distilled water. To assure its cleanness, the washed CCs were ultrasonicated in ethanol for 20 min followed by drying at 90 °C in a vacuum oven for 10 h.¹²

2.3. Synthesis of the PEDOT nanostructure (CC/PEDOT) electrodes

The growing of PEDOT on CC was performed by what is called ‘*in situ* hydrothermal polymerization’. In this method, 3,4-ethylenedioxythiophene (EDOT) was mixed with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol/water (1:1) mixture solution. The reactor was then heated up to 150 °C for 15 h into a sealed reactor followed by cooling to room temperature. After washing with water, the product was then washed with HCl to remove any unreacted ferric ions. Different mole ratios of EDOT/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1:1, 1:2.5, and 1:5) have been performed to prepare different (CC/PEDOT) electrodes and the performance of the three electrodes was compared with a pristine CC anode.¹³

For each run, the reactor was stirred for 20 min at ambient temperature and then, it was moved into an autoclave containing the CC films. This was followed by heating the sealed autoclave in a closed oven at 150 °C for 15 h to complete the hydrothermal polymerization process. After cooling down, the obtained modified films were washed with distilled water. The obtained CC/PEDOT electrodes were then immersed in conc. HCl to clean the excess of metal ions. Finally, the films were washed with distilled water, rinsed with ethanol, and dried at 90 °C for 12 h in a vacuum oven. The washing process was repeated three times to assure the purity of the obtained CC/PEDOT surface from any traces of iron (Fe) content.

2.4. Designing of microbial fuel cell (MFC)

Its configuration consists of an anode and an air-cathode with dimensions of 6 cm long and 5 cm in diameter with total working volume of $\cong 75$ milli.

The anodes were three-dimensional carbon felt that is fixed at the top of a port with dimensions ($2.5 \times 2.5 \times 0.5$ cm) and its area is about 18 cm^2 . In parallel to the cathode, they were positioned on the other side of the cell (a distance of ~ 5 cm).

The used cathode electrodes were of the type 'gas diffusion CC' with dimensions of 5×5 cm and surface area of 18 cm^2 and a catalyst amount of 0.35 mg/cm^2 . Titanium wires were used as current collectors for both electrodes. The current collector used for these electrodes were titanium wires.¹⁴

3. Results and discussion

3.1. Energy generation

In suitable microbial communities, specific reactions, known as bioelectrochemical reactions,

generate electricity in MFCs. These biological systems work to convert the chemical energy present in bacterial populations into electrical energy through the process of anaerobic metabolism.^{15,16} MFC contains both anode and cathode as shown in Fig. 1. This is a single-chamber cell design, and it is locally manufactured and purchased for this research.

This technique is simply described as follows: there is an oxidation process for the organic material occurs at the anode side while a reduction process (for oxygen) is occurring at the cathode side. These bioelectrochemical reactions produce energy.

The anode-respiring bacteria (known as electricigens) are the electroactive biofilms of MFC and have the ability to interact with the organic material (oxidation) and push the resulting electrons to the anode surfaces that are consequently moved in the wire circuit to the cathode. This is the characteristic definition of MFC. Due to this process, the produced protons move into the solution (producing $-ve$ potential at the anode) through the presence of the ion-exchange membrane, while oxygen will be reduced to give H_2O .¹⁷ This process has been performed using double-chamber MFCs (shown in Fig. 2), which are also locally manufactured and purchased for this research.

3.2. MFC configuration

The MFC design in which all studies were performed is shown in Fig. 2. This double-chamber design was used for all MFC studies as described elsewhere.¹⁸ Fig. 3 represents a series of MFCs connected in series for MFC studied (as an example).

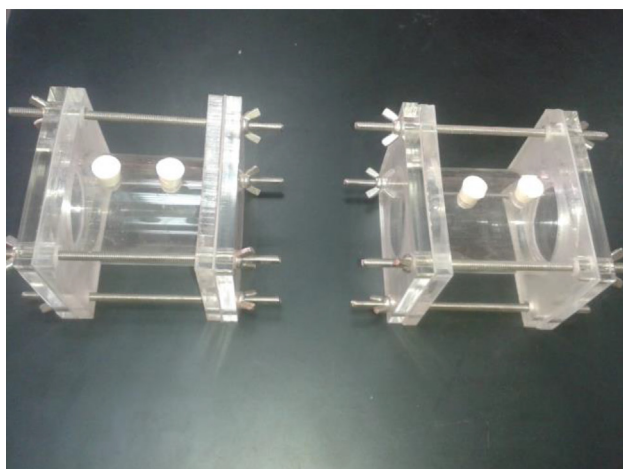
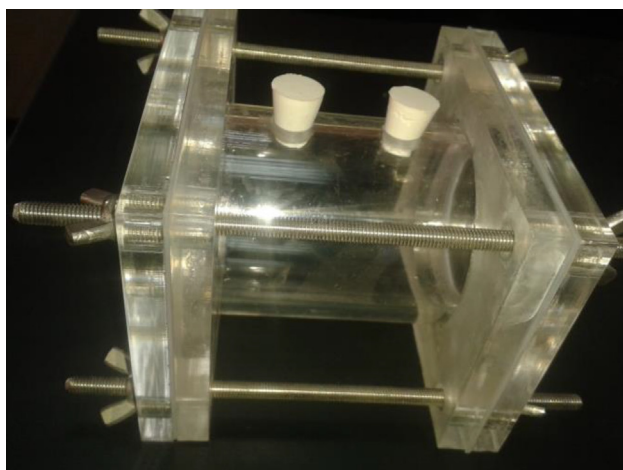


Fig. 1. Single-chamber microbial fuel cells.

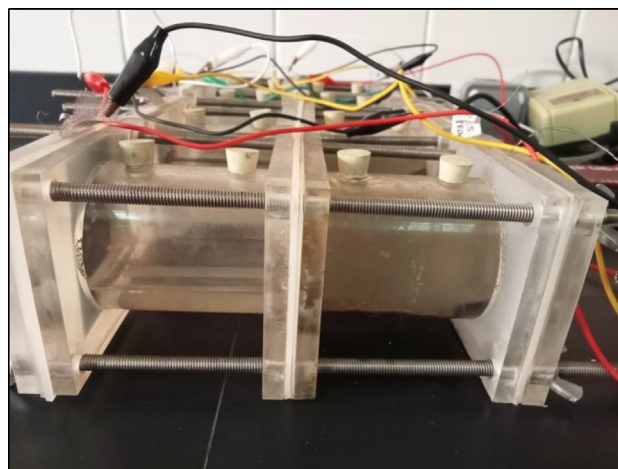


Fig. 2. Double-chamber microbial fuel cells.

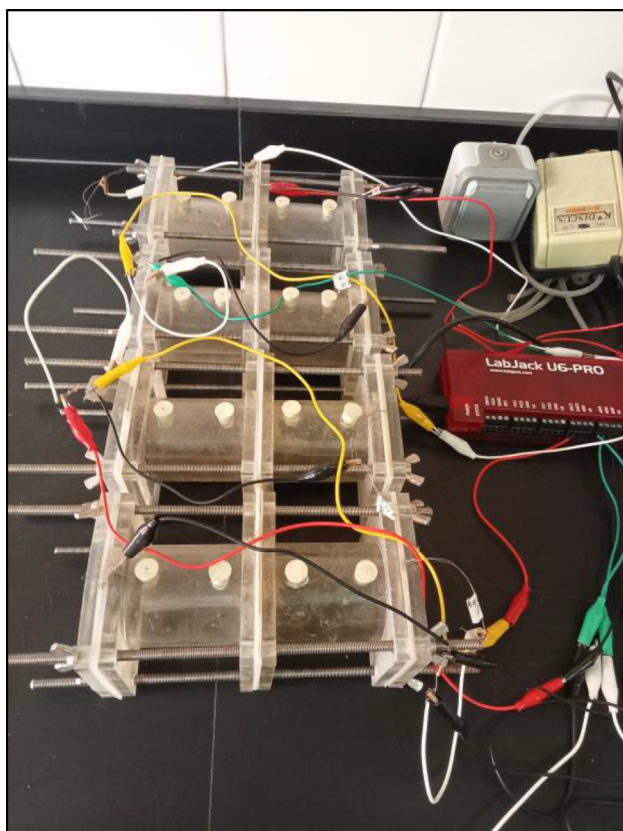


Fig. 3. Microbial fuel cells series configuration.

3.3. Modification of carbon cloth (CC) with PEDOT

To enhance the electrode conductivity to be suitable for electron transferring, CC material was treated with a well-conducting polymeric material, PEDOT. This polymer has been known for its unique uses as it is a good conductor of electricity.¹² The growing of PEDOT nanostructures on CC substrates was performed through a facile one-step hydrothermal method where all the run conditions and quantities are shown in Table 1.

3.4. MFC operation

At the beginning, 4 milli of a digestive sludge vaccine (digester sludge inoculum) was fed to the anode chamber.¹⁹ To form the biofilm on the anode,

the following media was injected: sodium acetate 1.5 g/L, potassium dihydrogen phosphate 1.024 g/L, potassium phosphate dibasic 7.3 g/L, and ammonium chloride 0.41 g/L. The cells were filled with sludge from a local water treatment plant and then operated for a few days to ensure biofilm growth on the anode surface.^{20,21} Considered as the organic substrate, sodium acetate (2.0 g/L) was dissolved in the wastewater with a phosphate buffer, a mineral, and a vitamin solution.

Bacterial systems are essential for the bio-electrochemical processes in these cells. In the anode chamber, exo-electrogenics oxidize organic material that produces electrons on the anode.²²

3.5. MFC performance

The performance of the MFC was studied during the start-up period by monitoring the electrical current intensity over time during batch operation of the cycles. Initially, the four MFCs were operated with an open circuit without using any resistors (shown in Fig. 3), and this was repeated for three cycles. Then, we repeated this test using several resistances and measured the output potential in each cycle that the cell can reach. In each cycle, sufficient time, ranging from two to seven days, was waited to allow the microbial community (the sludge used in the anode chamber) to undergo the fermentation process and obtain the appropriate potential. For this reason, several resistors were used in this study, 100, 500, 1000, and 2200 Ω , and for each resistance used, several cycles were achieved to confirm the results obtained. In the case of using resistances 100, 500, and 1000, the obtained potential at the end of the cycle was very low. In addition, these resistances did not give good results for PEDOT 1:5, which is supposed to give better results. But the results came on the contrary, as sometimes the control may have higher results than the PEDOT. This may be attributed to not using the appropriate resistor until this time or to failure of adjusting the operating conditions till this time. Therefore, it was necessary to try using another resistance that was much higher than what was previously used.

Table 1. Synthesis of the poly (3,4-ethylenedioxythiophene) nanostructure (carbon cloth/poly (3,4-ethylenedioxythiophene)) electrodes.

Run number	Chemical	Molecular weight MWt (g/mol)	Weight Wt (g)	No. of moles (Wt/MWt)	Mole ratio of EDOT/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
	EDOT	142.17	0.711	0.0050	1:0
1	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	270.29	1.4	0.0052	1:1
2			3.38	0.0125	1:2.5
3			6.7	0.0248	1:5

3.6. Resistance 2200

The 2200- Ω resistance was used and many cycles were done in order to reach the highest potential and the optimum operation conditions. For each cycle, the obtained potential was presented versus time for all PEDOTs (1:1, 1:25, 1:5, and control) as shown in Fig. 4. This figure shows the best three cycles that were made using the resistance 2200 Ω out of a total of 9 cycles that were performed.

The chart showed that PEDOT 1:5 was the best PEDOT concentration used than PEDOT 1:1 or PEDOT 1:2.5. In spite of that, the curve of PEDOT 1:1 seemed to be higher than that of PEDOT 1:5 but it is not the reality because the higher potential results of

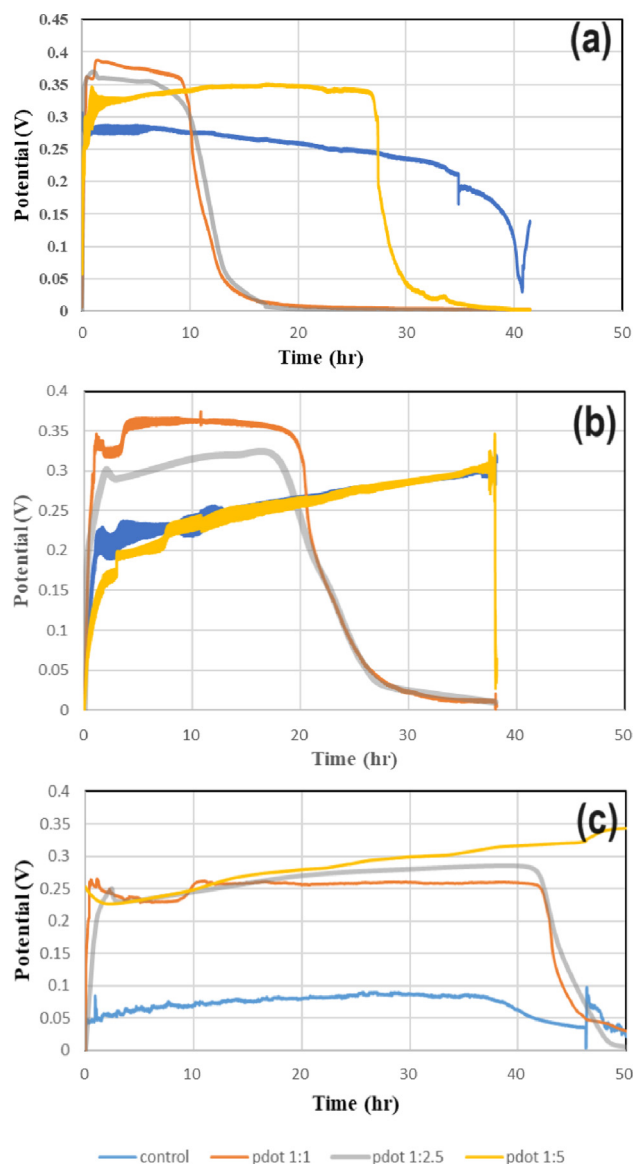


Fig. 4. Three cycles of resistance 2200 for the four microbial fuel cells.

PEDOT 1:1 were only for a short time and quickly the results go down, as shown in Fig. 4a and b. In contrast, the result line of PEDOT 1:5 showed high potential results for a long time before going down as shown in Fig. 4c. This result explains that the higher concentration of PEDOT, the higher potential yield obtained.

3.7. Desalination process

The MDC in which desalination process was performed is shown in Fig. 5. In this process, MDC was designed to have three compartments separated physically by cation- and AEM that were previously prepared in other work.^{10,11} These three chambers are designed as anode, cathode, and the middle chamber was dedicated to the water desalination (as schematically illustrated in Fig. 5). The anode chamber was separated from the middle chamber by a CEM. On the opposite side, the cathode chamber was separated from the middle chamber by an AEM.

The selected anode chamber was PEDOT 1:5 that was the optimal one in Fig. 4c. It was activated as

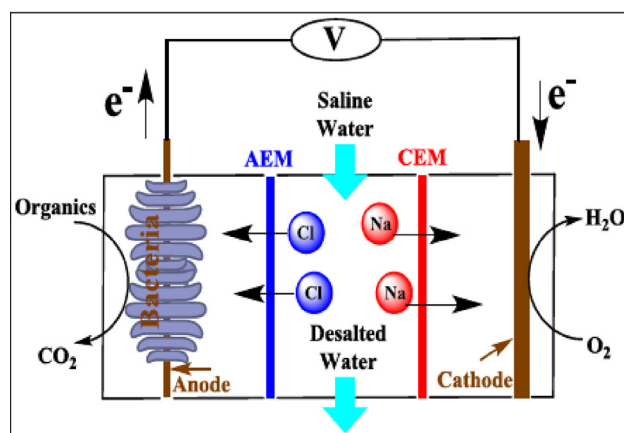
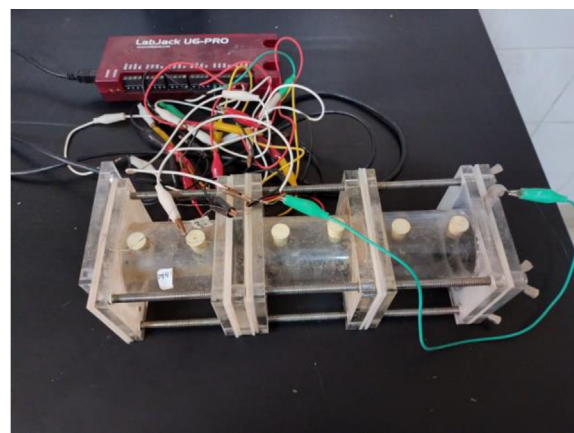


Fig. 5. Triple-chamber microbial desalination cell.

discussed above. Sodium chloride solution in concentration of 30 g/L (as seawater) was inserted in the middle chamber. In such setting up for the desalination process, the conductivity on both anode and cathode chambers was obtained. The average conductivity of anode chamber was 8.2 mScm^{-1} , while it was 6.1 mScm^{-1} for the cathode chamber. This choice was dictated in order to increase the diffusion of water between the middle chamber and the other two chambers (anode and cathode).

MDC were run in a separate mode (batch) and connected to resistances of 500, 1500, and 2200 Ω for a period of 2 days (Fig. 6). The measurement was performed by recording the potential voltage using a datalog system. A small specimen from each chamber was periodically syringed to measure the conductivity and the pH value, then, each specimen was reinjected into its position chamber to keep the condition (concentration) stable. This process was periodically repeated for 48 h. In this process, the polarization curves for the MDC were obtained through linear sweep voltammetry (LSV) using the 3-electrode configuration. In this configuration, the working electrode was the cathode and the counter electrode was the anode in addition to a reference that was short-circuited with the counter electrode. The potential voltage versus time are presented in Fig. 6 from which it can be seen that the highest-obtained potential was achieved when using the 2200 resistance.

The measuring range for the polarization curves was performed between open-circuit voltage and 0 mV. In this case, the relationship $P=V \times I$ was used to obtain the power curves.

The desalination process has been performed by running the MDCs for 48 h. It could be noticed that when the used resistances were 2200, 1500, and 500 Ω , the cell voltages recorded were 0.4–0.45 V, 0.1–0.15 V, and 0.01–0.02 V, respectively (Fig. 6). In addition, the polarization and power curves measured initially showed a power peak of $\approx 0.5 \text{ W/}$

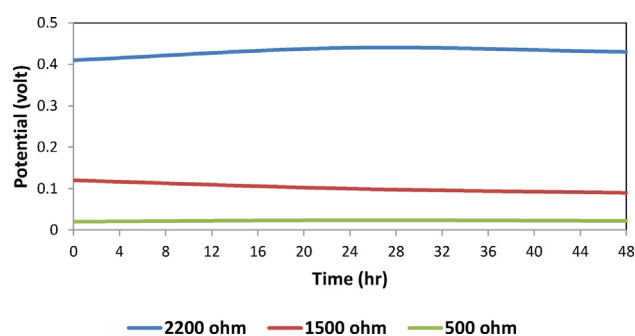


Fig. 6. Potential versus time measured over resistances of 2200, 1500, and 500 Ω for a period of 48 h.

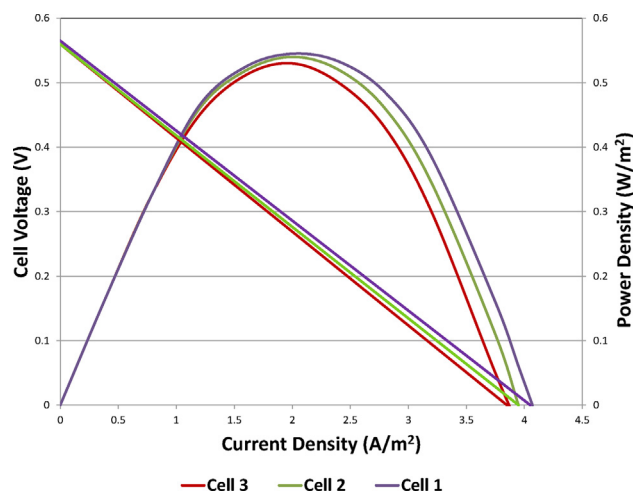


Fig. 7. Power curves taken at the beginning of the experiments.

m^2 and a maximum current achieved of $\approx 4.2 \text{ A/m}^2$ (Fig. 7).

The desalination process was followed-up by measuring the solution conductivity inside the desalination chamber. This test was periodically

Table 2. Solution conductivity of the desalination chamber in a time period of 48 h.

Time (h)	Solution conductivity (mScm^{-1})		
	2200 Ω	1500 Ω	500 Ω
0	49	50	50.2
4	43.5	45.5	46.5
8	39	41.5	42.5
12	34	37	38.5
16	30	33	35
20	26	29	31.5
24	23	26	28.5
28	21	24	25.5
32	19.5	22	24
36	18.5	21	23
40	18	20	22.3
44	17.7	20	22
48	17.5	20	21.8

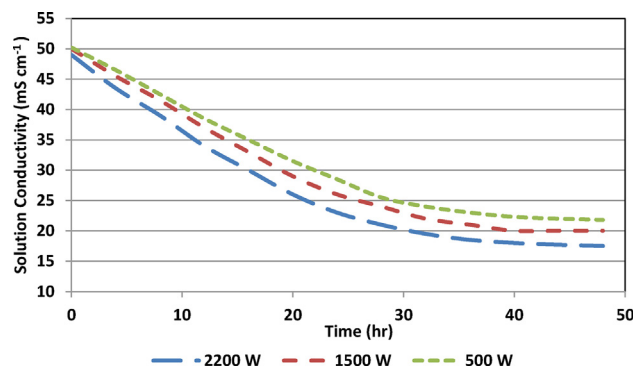


Fig. 8. Solution conductivity of the desalination chamber.

performed for 48 h, one measure per each 4 h. The solution conductivity data are illustrated in Table 2 and are presented in Fig. 8.

It could be noticed from this figure that the solution conductivity significantly decreased from 50 to about 20 mScm^{-1} in 48 h. This means that about 60% of the salt has successfully been removed from the desalination chamber in a time of 48 h. The process was repeated at different resistances (2200, 1500, and 500Ω) to check the desalination rate at each resistance. It was found that the salt removal happened independently and it has not been affected by the resistance value, indicating that the reaction and the current produced was not the main driver of the desalination process.

4. Conclusions

PEDOT nanostructure was successfully grown on the CC film via *in situ* hydrothermal polymerization to enhance the electrode conductivity to be suitable for electron transferring. This modification was performed using a polymeric material that is conductive: PEDOT. The modified CC/PEDOTs were simply constructed to build up cost-effective microbial water desalination cells (MDCs). Three different mole ratios of EDOT/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1:1, 1:2.5, and 1:5) have been performed to prepare three different PEDOT electrodes followed by characterization. The obtained potential was presented versus time for all PEDOTs (1:1, 1:2.5, 1:5, and control). It was found that PEDOT 1:5 showed the highest potential result for a long time before going down. As a result, the chart showed that PEDOT 1:5 was the best PEDOT concentration ratio.

From the results of the desalination process, it is clear that the prepared MDC cells have the ability to remove up to 60% of salts. The solution conductivity significantly decreased from 50 to about 20 mScm^{-1} in 48 h. Consequently, desalination process has successfully occurred and the configuration of the proposed desalination cell (MDC) is effective for salt removal.

Therefore, as the demand of this work, a new MFC) has been configured by combining polymerically modified electrodes and selective membranes (AEM and CEM). This was followed by the desalination process in which a new bio-electrochemical process has successfully produced electricity from the produced electrons during biological reactions of bacteria.

These results are a proof of concept for the aim of this work. As a future aspect, the obtained desalination value in this work could be increased by reusing freshly washed membranes: AEM and CEM

to remove bound ionic salts. As a consequence, detailed water analysis like chemical oxygen demand specific desalination rate (SDR), total desalination rate (TDR), and pH could be quantitatively obtained.

Conflicts of interest

There are no conflicts of interest.

Acknowledgements

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