Desalination of seawater using an electrode modified with poly(3,4-ethylenedioxythiophene)

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Abstract. The procedure for obtaining electrodes modified with poly(3,4-ethylenedioxythiophene) has been widely studied for its multiple applications. This study evaluates the potential contribution of electrodes modified with poly(3,4-ethylenedioxythiophene) for desalination of seawater. Potentiostatic electropolymerization of 3,4-ethylenedioxythiophene was conducted on 6 cm² steel electrodes by using a supporting electrolyte consisting of lithium perchlorate in acetonitrile. This modified electrode was used in the extraction of anions and cations from samples of synthetic seawater by means of 20 extraction cycles (optimal cycles) and using a combination of p-type and n-type doping. A total of 140 extractions (number of optimal extractions) were carried out, which led to desalination of synthetic seawater by about 80-90%, as evidenced by the decrease in the conductivity of the solution containing the ions. Therefore, this procedure could become an alternative for seawater desalination.

1. Introduction
Desalination is a process used to remove minerals from water in order to make it suitable for human consumption. Currently, this process is carried out by using methods such as reverse osmosis, distillation, freezing, flash evaporation, hydrate formation, and electrodialysis, among others [1-4]. However, issues such as the high costs related to infrastructure and production can become a major obstacle to the implementation of these procedures.

Therefore, this paper focuses on promoting the use of a device consisting of a steel electrode containing a conductive polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), that can be doped using reversible p- or n-type doping [5-7]. Additionally, it can be used to manufacture a number of artifacts including supercapacitors, organic light-emitting diodes (OLEDs), solar cells, electrochromic devices and electrochemical sensors [8-14].

Doping refers to the process through which oxidation is achieved by a concomitant change in the electronic properties of the material thus providing it with metallic-type conductivity due to charge delocalization which leads to the formation of polarons and bipolarons [15-17]. P-type doping of polymers refers to partial oxidation, which is shown in Equation (1).
A counter-anion must be added in order to ensure the electroneutrality of the system. This process is represented by Equation (2).

\[
[(\text{CH}^\text{y+})_x + (\text{xy}) \xrightarrow{\text{A}} [(\text{CH}^\text{y-})_x \text{Ay}^-]\text{,}
\]

The reduction, which is the opposite of partial oxidation of the polymer and is associated with type-n doping, is shown in Equation (3).

\[
(\text{CH})_x + (\text{xy}) \xrightarrow{\text{e}^-} [(\text{CH}^\text{y-})]_x
\]

This process involves the use of a cation in order to maintain the electroneutrality of the system, as shown in Equation (4).

\[
[(\text{CH}^\text{y-})]_x + (\text{xy}) \xrightarrow{\text{M}^+} [(\text{M}_y^+ + (\text{CH}^\text{y-})]_x
\]

Since this is a reversible process, the application of a specific electric potential to the polymer matrix will result in the dopant entering or leaving the polymer thus allowing to maintain electroneutrality [18,19]. Doping can be carried out by using techniques such as the electrochemical method, which allows to perform a highly controllable and reproducible process as well as proper adjustment and monitoring of charge transfer [20]. There is a proportional relationship between the amount and type of the dopant used and the polymer conductivity, which also affects the structural properties of the polymer (color, porosity and volume) [21-24]. When doping is performed, the polymer used can be either positive or negative, which could facilitate insertion of cations and anions into the polymer matrix.

The aforementioned property is an important factor considered in this study due to its potential utility in the development of a device for effective cation and anion extraction. Factors such as the use of p-doped polypyrrole for the extraction of arsenate and copper complexes, as well as the use of n-doped PEDOT as a tool to detect and remove mercury, were also considered in this study [25-29]. According to the above mentioned and in order to take advantage of the properties of both p-type and n-type doping of PEDOT [5,28] Figure 1(a) and Figure 1(b) show how the extraction of cations and anions from artificial seawater would be carried out.

Figure 1(a) shows that when n-type doping is used, the cations are inserted into the polymer matrix, and subsequently released when the matrix is positively charged. Figure 1(b) shows the opposite process using p-type doping. Both cases result in extraction of the ions of interest.

**Figure 1.** Schematic representation of the proposed model for the process of extraction of cations, based on the (a) n-doping and n-undoping, and (b) p-doping and p-undoping, process of conductive polymers (CP).

2. **Experimental**

The equipment, reagents and methods used in this experimental development are described below.
2.1. Preparation and characterization of poly(3,4-ethylenedioxythiophene) - modified electrodes

First, the optimization of electrochemical oxidation of 3,4-Ethylenedioxythiophene (EDOT) on steel was carried out in order to obtain a polymer deposit of PEDOT with n-doping-undoping suitable for the proposed process. Electrochemical measurements were performed on an AISI 316 steel disc (0.07 cm²) using a spiral-shaped platinum wire as an auxiliary electrode, as well as an Ag|AgCl wire in tetramethylammonium chloride whose potential matches that of saturated calomel electrode (SCE) - at room temperature - as a reference electrode [30]. Electropolymerization of EDOT (97%, Aldrich) was performed using a VoltaLab PGZ 100 potentiostat (Radiometer Analytical) by successive potentiodynamic sweeps (cyclic voltammetry), at a sweep speed (v) of 50 mV.s⁻¹ from solutions containing different monomer concentrations with various supporting electrolytes and potential windows. The optimal conditions for the purposes of this work were set as follows: a concentration of EDOT (0.01 mol. L⁻¹) and lithium perchlorate (LiClO₄, 99.99 %, Aldrich) 0.1 mol·L⁻¹ as a supporting electrolyte in CH₂CN, and a potential window of -1.0 V to 1.5 V. The potentiostatic method was also tested. The results suggest that 1.4 V is the most suitable potential to prepare stainless steel/poly(3,4-ethylenedioxythiophene) (SS/PEDOT)-modified electrodes.

Each case showed a stable electrochemical response of the SS/PEDOT in a solution containing the supporting electrolyte by which the electrochemical responses of the p-type and n-type doping of the polymer were obtained. The measurements were performed at room temperature (20 °C) using high purity argon in 3-compartment anchor cells. Once the adequate conditions to prepare SS/PEDOT were determined, a BAS SP-2 potentiostat was used along with the aforementioned solutions in cells and electrodes such as those already described. On the other hand, the geometrical area of the working electrode was increased by 6 cm² via the potentiostatic method, by applying a potential of 1.4 V for 20 minutes. After the preparation of the SS/PEDOT, the ion extraction process was carried out through successive extraction cycles (ExC).

2.2. Preparation of artificial seawater

All solutions were prepared using freshly deionized water via a heat force deionizer. Artificial seawater was prepared according to ASTM D1141-98 [31], by using three stock dilutions as follows:

2.2.1. Stock solution #1. The stock solution #1 (St-S1) is prepared by dissolving 55.5 g of MgCl₂·6H₂O together with 5.7 g of CaCl₂ and 0.21 g of SrCl₂·6H₂O in 100 ml of deionized water.

2.2.2. Stock solution #2. This solution #2 (St-S2) is prepared by dissolving 6.95 g of KCl together with 2.01 g of NaHCO₃; 1.00 g of KBr; 0.27 g of H₂BO₃; and 0.03 g of NaF in 100 ml of deionized water.

2.2.3. Stock solution #3. Stock solution #3 (St-S3) contains metallic ions and is prepared by dissolving the corresponding salts in 100 ml of deionized water as follows:

- Ba(NO₃)₂: 0.0994 g; Mn(NO₃)₂: 0.0546 g; Cu(NO₃)₂: 0.0396 g; Zn(NO₃)₂: 0.0151 g; Pb(NO₃)₂: 0.0066 g; Ag(NO₃)₂: 0.0004 g.

Stock solutions 1, 2 and 3 are used to prepare a solution consisting of 500 ml of artificial sea water (S-SW) in deionized water composed of 12.267 g of NaCl; 2.270 g of Na₂SO₄; 10 ml of St-S1; 5 ml of St-S2; and 0.5 ml of St-S3. The pH level is adjusted to 8.2 using a standard sodium hydroxide solution (0.1 mol·L⁻¹).

2.3. Ion extraction process

This study involved the use of successive extraction cycles (ExC) that are performed by placing the SS/PEDOT in the cell A - containing artificial seawater (S-SW) - and then perturbed via a potentiostat at the n-doping potential of the polymer (-1.0 V) for 5 minutes. The electrode is then placed in cell B which contains deionized water and perturbed at n-undoping potential (0.3 V) for 5 minutes. This process (ExCn) is carried out successively (20 times) after which a 30-second perturbation at the p-
doping potential of the polymer (1.0 V) is performed in cell A. Then the electrode is brought back to cell B and subjected to perturbation at p-undoping potential (-0.1 V).

The p-doping/p-undoping ExCp cycle is conducted only once and after it, the “cycle n-doping/n-undoping, ExCn” is conducted for another 20 successive times. This process was repeated until ExCnp process was completed, this consisted in performing a total of 140 n-doping successive extractions, alternating with a p-doping type extraction. The p-doping/p-undoping (ExCp) cycle is done only once, followed by 20 successive series of the n-doping-undoping cycle (ExCn). This process was repeated until the ExCnp cycle was completed. This last cycle consisted of a total of 140 successive n-doping extraction sessions along with a p-doping type extraction.

2.4. Characterization by other techniques
The concentrations of cations in artificial seawater were determined in cells A and B, before and after the extraction processes, by inductively coupled plasma atomic emission spectroscopy (ICP-AES) via a Varian Liberty Series II spectrophotometer. The electrical conductivity of the solutions contained in cells A and B was also measured during the extraction process by using a Multifunction Meter Cx-701.

3. Results
Results of the experimental procedures are detailed below.

3.1. Preparation of stainless steel/poly(3,4-ethylenedioxythiophene) modified electrodes
Figure 2(a) shows the voltammetric profile associated with the electrochemical oxidation of EDOT when subjected to 50 successive potentiodynamic cycles under the experimental conditions described above and proper potential window. The increase in the current as well as the presence of p-doping (in the area between 0.0 V and 1.0 V) and n-doping processes (in the area between 0.0 V and -1.0 V) demonstrate the growth of the polymer [32]. In addition to being associated with p-doping-undoping and n-doping-undoping processes, these profiles allow to determine the area where nucleation and growth occur (around 1.5 V) [32]. Therefore, the optimal potential to carry out the potentiostatic method can be determined from this data as shown in Figure 2(b).

The i/t waveforms in Figure 2(b) show an increase in the current and the subsequent exponential decay until reaching the nucleation point which causes the growth of the deposit (induction time). The subsequent increase in the current is directly related to the growth of the deposit. Therefore, this shows that the use of potentials less than 1.4 V will result in a very high induction time, while higher potentials cause a low and erratic induction time, thus leading to total loss of reproducibility and overoxidation of the film. This also shows that 1.4 V is the most suitable value for electropolymerization of EDOT by potentiostatic method in the other experimental conditions used in this study.

Figure 2. (a) EDOT Voltammetric profiles 0.01 mol·L$^{-1}$ + LiClO$_4$ 0.1 mol·L$^{-1}$ in CH$_3$CN, during electropolymerization on a SS disc of 0.07 cm$^2$ ($v = 50$ mV·s$^{-1}$), through successive potentiodynamic cycles (number of cycles is indicated above respective answers). (b) Transients j/t registered during electropolymerization of EDOT by the potentiostatic method (E are indicated in the inset). Interface: SS/0.01 mol·L$^{-1}$ EDOT + 0.1 mol·L$^{-1}$ LiClO$_4$, CH$_3$CN.
Figure 3(a) and Figure 3(b) show the electrochemical responses occurring in the p-doping-undoping and n-doping-undoping areas of SS/PEDOT electrodes prepared according to the conditions described above. These responses allow to determine the potential use of polymeric deposits in cation exchange processes since both processes are reversible, p-type doping occurs around 1.0 V. This value will be used for the extraction of anions. On the other hand, type-n doping, which is used for cation extraction, occurs around -1.0 V.

Figure 3. (a) Response in the zone of potential of p-doping-undoping of SS|PEDOT in LiClO$_4$ 0.1 mol·L$^{-1}$ in CH$_3$CN. (b) Response in the zone of potential of n-doping-undoping of SS|PEDOT in LiClO$_4$ 0.1 mol·L$^{-1}$ in CH$_3$CN.

3.2. Seawater desalination

Figure 4(a) and Figure 4(b) describe the conditions and methods used in this study to remove ions from artificial seawater.

Figure 4(a) and Figure 4(b) provide a general overview of the cation-ion extraction process. When reduction potential is applied as shown in Figure 4(a), the cations in cell A migrate towards the polymer film [19,33,34], thus facilitating extraction. When the electrode moves to cell B and oxidation potential is applied, the cations are repelled by the polymer film and released into the cell. When oxidation potential is applied as shown in Figure 4(b), the anions in cell A migrate towards the polymer film [19,33,34], thus facilitating extraction. When the electrode moves to cell B and oxidation potential is applied, the anions are repelled by the polymer film and released into the cell.

Table 1 shows the initial and final quantities obtained for species present in artificial seawater (D-SW) before and after the extraction process. The extraction percentage for each cation is also determined from these data.

Table 1 suggests that the use of n-doped/n-undoped and p-doped/p-undoped polymers could result in successful desalination of artificial seawater as demonstrated by the extraction percentages achieved.
This Table 1 shows a decrease in the initial cation concentrations when the extraction process is applied, as demonstrated by comparing the initial and final concentrations. The table also shows the percentage of extraction for each of the cations.

This indicates that the PEDOT polymeric matrix could be more suitable to carry out this process. Furthermore, as shown in Table 2, charge tracking and process monitoring by electrical conductivity in cells A (Ion extraction cell) and B (Ion release cell), allow to determine the ion exchange effect as a result of the extractions.

Table 1. Measures of initial concentration and final concentration of synthetic seawater.

| Cation | Initial (mg/L) | Final (mg/L) | Extraction (%) |
|--------|----------------|--------------|----------------|
| Ag     | 0.49           | 0.01         | 38.70          |
| B      | 270.00         | 0.26         | 99.71          |
| Ba     | 99.40          | 0.08         | 99.97          |
| Ca     | 579.00         | 21.50        | 99.00          |
| Cu     | 39.00          | 0.12         | 90.52          |
| K      | 3950.00        | 30.10        | 88.64          |
| Mg     | 1110.00        | 11.00        | 99.97          |
| Mn     | 54.60          | 0.19         | 89.56          |
| Na     | 24534.00       | 339.80       | 99.97          |
| Pb     | 66.00          | 0.03         | 86.36          |
| Sr     | 140.00         | 2.49         | 98.21          |
| Zn     | 0.50           | 0.46         | 8.60           |

Table 2 shows that successful desalination of seawater occurs when electric conductivity is 1.10 mS·cm⁻¹ after the completion of the extraction cycle. This value is close to that of the conductivity of drinking water, since according to the existing literature, the value of the electrical conductivity of the water must be in the range between 0.20 - 1.10 mS·cm⁻¹ in order to be considered potable [35]. Figure 5 shows the decrease in conductivity occurring in cell A (Ion extraction cell) while there is an increase in the conductivity value in cell B (Ion release cell), showing that the proposed extraction process is actually occurring.

Table 2. Measures of electrical conductivity in cells during extraction stages in the “desalination”.

| Day | Cell A (mS·cm⁻¹) | Cell B (mS·cm⁻¹) | # Extractions |
|-----|------------------|------------------|--------------|
| 0   | 59.00            | 0.00197          | 0            |
| 1   | 24.10            | 18.05            | 40           |
| 2   | 15.00            | 24.05            | 20           |
| 3   | 10.15            | 31.36            | 20           |
| 4   | 5.07             | 37.67            | 20           |
| 5   | 2.91             | 43.95            | 20           |
| 6   | 1.10             | 44.92            | 20           |

Figure 5. Electrical conductivity in cells A (Ion extraction cell) and B (Ion release cell) during “desalination” process.
4. Conclusions
Desalination of artificial seawater was effectively accomplished in this study according to the results obtained from conductivity measurements showing a reduction in the initial value in cell A until reaching a value of 1.10 mS.cm\(^{-1}\). This indicates that desalination was achieved by 80-90%. The results show that the process has proven to be efficient and shed light on the possibility of using PEDOT modified electrodes as well as n-doped/p-doped conductive polymers as an appropriate tool for the extraction of cations and anions. In addition, it paves the way for further research on this groundbreaking modified electrodes as well as n-doped/p-doped conductive polymers as an appropriate tool for the extraction of cations and anions.

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