New energy sources: blue energy study in Central America

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Blue energy or salinity difference energy takes advantage of the free energy released in the mixture of two solutions with different salinity concentrations as it happens continuously in river mouths. Among the large number of available techniques that aim to harness blue energy, capmix (or capacitive mixing) methods allow to directly extract electrical energy without the need of any electromechanical converter such as turbines or heat engines. The main goal of this article is to analyze the potential of blue energy by capmix methods in Central America. So far, blue energy studies have been principally carried out in countries from the global North. Therefore, we describe experimental results with real sea and river waters from the Gulf of Fonseca, an area of special interest due to its hydrographic richness, which is situated among Honduras, El Salvador and Nicaragua. An electrochemical cell, which consists of a pair of activated carbon electrodes coated with cationic and anionic polyelectrolyte layers respectively, is used in the experiments. The cell voltage in open circuit (OCV) is used as a measure of the performance of the capmix process. It is found that the OCV is larger when natural river water is used instead of low salinity NaCl solutions. The rainy season in which the experiments were performed reduced the ionic content of the river, increasing the salinity difference with ocean waters. The feasibility of capmix as a means of clean energy production is discussed.

Keywords: Blue energy, Capmix techniques, carbon electrodes, polyelectrolyte coating

I. INTRODUCTION

The production of electrical energy from renewable sources is an immediate challenge in our world, where current global production of electricity is seriously harming the environment of our planet. Scientific research is leading this challenge towards finding new energy sources and optimizing the existing ones. Although solar and wind energy are outstanding among all renewable energies in terms of efficiency, in recent past other alternatives have been growing in importance. Specifically, the proposal initially published in the 1950's[1] and later in the 1970's[2–4] suggests how the considerable difference in salinity between sea and fresh waters (500 mM and 20 mM, roughly) could be used in the generation of electricity. The sources of renewable energy that take advantage of this salinity difference are collectively known as blue energy.

In river mouths, for instance, the mixing of a certain volume of low salinity water concentration (expressed as c_1) with a much larger volume of salt water (c_2 concentration) is continuously taking place. According to thermodynamics, the spontaneous mixing of ions of sea water and river water produces an entropy increase and hence, a free energy decrease. In other words, the rise in concentration of the fresh water in the process results in an increase of its osmotic pressure (Δp) up to the sea water value, $\Delta p = (c_2 - c_1)RT$, which amounts to 10 atm per type of ion (about 20 atm for NaCl solutions). Therefore, the energy loss (which we partially aim to use) would be $\Delta pV \approx 2$ kJ per liter of water mixture. If we focus on El Salvador and assume that the whole Lempa river volume flow (on average 175 m^3/s) could be employed for this purpose, the available power would exceed 300 MW (almost one quarter of the installed power in El Salvador, according to SIGET data, www.siget.gob.sv). Similarly, for the whole planet, it is estimated that the total available power from blue energy sources would be 2 TW, which roughly coincides with the annual electricity demand.

In order to extract this energy, current research is focused on finding efficient methods. Among them, the membrane-based techniques are the most advanced ones: pressure retarded osmosis (PRO)[5,6] and reverse electrodialysis (RED)[7,8]. PRO generates an osmotic pressure difference between two chambers in order to produce pressurized water to generate electricity through a hydroturbine, as it shown in Fig. 1 left. RED, on the other hand, creates an electrical potencial difference between the electrodes of a cell where dilute and concentrated solutions flow separated by cationic and anionic exchange membranes alternatively (see Fig. 1 right).

Despite the considerable progress made in those techniques[9–11], these are mostly at laboratory scale. Furthermore, they have some disadvantages that should still be solved to move towards commercialization, particularly in relation to membranes performance and cost in the case of RED, and the need to use electromechanical converters, like dynamos or turbines in PRO.

In this context, alternative approaches have recently emerged, in particular those presented in this paper

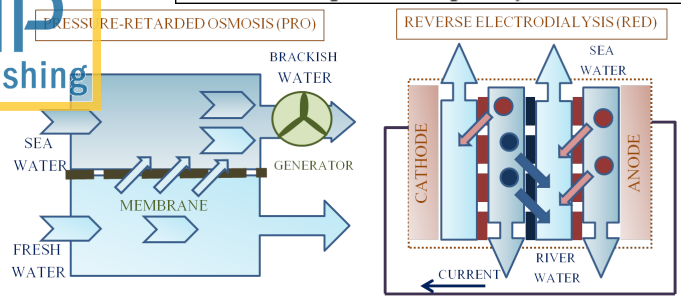

FIG. 1. Sketch of the membrane-based techniques PRO (left) and RED (right)

and called capmix techniques. There are principally two of them, known as CDLE (capacitive energy extraction based on double layer expansion methods)[12,13] and CDP (capacitive energy extraction based on Donnan potential)[14,15]. In the first case, the starting point is the consideration that the electric potential at the solid/ionic solution interface increases (if charge is constant) when decreasing the ionic strength of the medium. This property is widely known in the science of colloidal systems and interfaces and is due to the characteristics of the electrical double layer (EDL). Most colloidal particles are electrically charged, as can be readily demonstrated by detecting their motion in an electric field. When solid particles are dispersed in a polar solvent, in particular in an electrolyte solution, they acquire an electrical surface charge. From a distance, the charged colloidal particle appears to be electrically neutral. However, the surrounding ions are able to move under the influence of the thermal diffusion so that the region of charge imbalance, due to the presence of the particle, can be quite significant relative to the size of the particle itself. The arrangement of electric charges on the particle, together with the balancing charge in the solution, is called electrical double layer.

The capmix techniques are based on the fact that the EDL can accumulate a great amount of charge if the surface area is large enough, and also that its capacitance significantly depends on the ionic content of the medium. In Fig.2 left it is shown a sketch of the working principle of CDLE. Initially, ions are stored on the electrodes by means of an external voltage source or battery. After introducing fresh water in the capmix cell, voltage increases between the electrodes and an electrical current can spontaneously flow. Since this transfer is performed at a higher potential, we obtain more energy than that initially extracted from the battery, resulting in a positive balance of energy. Hence, the result is that electrical work is made available, without use of any kind of either selective membranes or electromechanical converters. In the CDP method (see Fig. 2 right), the electrode interfaces are loaded without any external power supply. In this case, the voltage difference generation involves the use of ion selective membranes on each electrode, and the cell potential is controlled by the Donnan potential difference. In principle, the CDLE approach would be cheaper and easier to implement because of the absence of membranes. Despite this, the problems of self-discharge of the cell have prevented real progress of this technique[16].

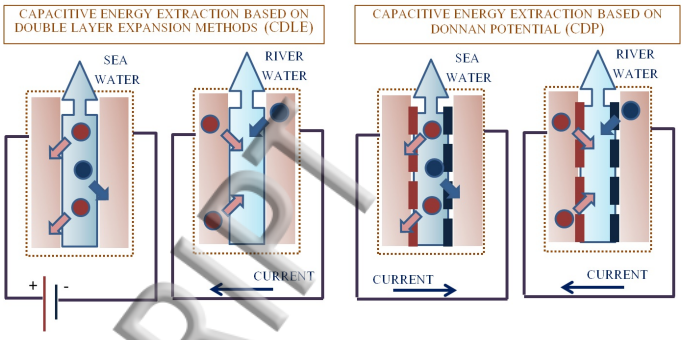

FIG. 2. Sketch of the working principles of the capmix techniques CDLE (left) and CDP (right).

Other proposed technique to access the energy from salinity differences is the *battery mixing*. This method is similar to capmix but instead of inert porous electrodes, mixing entropy batteries utilize reactive electrodes to extract blue energy by storing it as chemical energy[17]. Among capmix techniques, the latest research has developed new methods that combine aspects of both CDLE and CDP original technologies, mainly avoiding membranes by the modification of the bare activated carbon electrodes. Promising results have been found by the chemical treatment of the electrodes either by introducing charged molecules which remain permanently attached to the surface of the activated carbon[16] or by the concentration of strong acid surface functional groups to chemically modify high capacitance carbons[18]. The method that we propose in this work is based on conductive electrodes made of an activated carbon core and a polyelectrolyte layer, either cationic or anionic for each electrode, respectively[19]. We can attribute the term *soft* electrodes method or SE to this new method, which takes advantage of the spontaneous generation of a potential, as CDP, but avoiding the use of membranes, as CDLE. It is based on the physicochemical modification of two activated carbon electrodes by means of oppositely charged layers of polyelectrolyte (Fig. 3). Thus this method reduces the energy loss problem in CDLE, and avoids the use of ion exchange membranes resulting in a reduction of costs.

This article presents the results of a blue energy experimental study by the soft electrode capmix technique with the aim of analyzing the potential of this technique in Central America regions. We use real sea and river waters taken from the Gulf of Fonseca chosen because of its hydrographic richness. It is a protected area of the Pacific Ocean, located in the midle west of Central America, among Nicaragua, Honduras and El Salvador (see Fig. 4 left). Sea water at the entrance of the Gulf is characterized by a high salinity, about 35 g/L. Upstream,

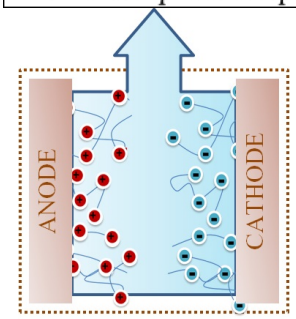

FIG. 3. Sketch of the capmix cell for the soft electrode method.

on the contrary, it is found a huge salinity decrease down to 1 or 2 g/L[20]. This fact makes the Gulf of Fonseca an ideal place for blue energy studies. Although it is out of the scope of this article, an ecological potential study[21] would also be needed to calculate the amount of usable water that can be transported to a salinity difference plant taking account of the ecological implications of altering the hydrodynamics of the marine environment.

FIG. 4. Left: Map of the Central America. Right: map of the Gulf of Fonseca where fresh water samples (light blue) and sea water samples (dark blue) were taken.

II. MATERIALS AND METHODS

The capmix cell that was used in this experimental study has been described elsewhere[22,23]. It is formed by two parallel graphite collectors coated by commercial activated carbon films (Voltea B.V., Netherlands), as shown in Fig. 5 top. The two electrodes, of about 3 cm^2, are placed facing each other at a distance of 600 μm.

Both sheets of activated carbon film were treated with cationic and anionic polymer solutions, producing respectively positive and negative surface charges on each one. For this purpose, Voltea films were kept in contact with 100 mM solutions of anionic and cationic pol-

FIG. 5. Top: sketch of the graphite collector and the piece of activated carbon film placed on it. Bottom: schematics of the capmix cell in which the two electrodes face each other.

electrolytes for 12 hours under magnetic stirring. After that time, the electrodes were rinsed with deionized water, and placed in the cell as shown in Fig. 5 bottom. The polymers used were cationic PDAMAC (poly (diallyldimethyl ammonium chloride)), and anionic poly (sodium 4-styrenesulfonate) or PSS, with molecuar weights 100,000 g/mol and 200,000 g/mol respectively.

The performed experiment measures the potential evolution between both electrodes of the capmix cell as a function of time during open circuit, that is, fresh water and salt water are passed alternately while the potential is recorded. All the measurements have been slightly shifted to zero in order to allow for the comparison among the different water samples. It should be recalled that these open circuit measurements reveal the potential application of this technique for different real situations. The so-called voltage rise (that is, the voltage elevation when solutions are exchanged) is determinant of the energy and power per cycle (note that the power is roughly proportional to the square of the voltage rise), which ultimately define the feasibility of the method. Ideally, this quantity would be a measure of the Donnan potential variations on both electrodes when the solutions are exchanged. However, this is not the case in general, and the rise depends on how efficiently the solution exchange takes place, how much charge is lost during the rise, etc., and this can change from one electrode to another or from one carbon material to another.

Three samples of river water were taken in: El Rebalse, Amatillo river and Pavana river, as shown in the map of Fig. 4 right in light blue. Seawater was taken in Puerto de la Union, as indicated in the same figure in dark blue. Moreover, solutions used as references were prepared at the laboratory with concentrations 30 g/L and 1 g/L sodium chloride.

III. RESULTS AND DISCUSSION

Fig. 6 shows the time evolution of open circuit voltage difference (OCV) between the electrodes of the capmix cell in Fig.5 when fresh water and salt water are successively introduced. As it is shown, the voltage rise between both solutions is approximately 120 mV, which is the maximum potential that will be used on a capmix cycle for energy extraction.

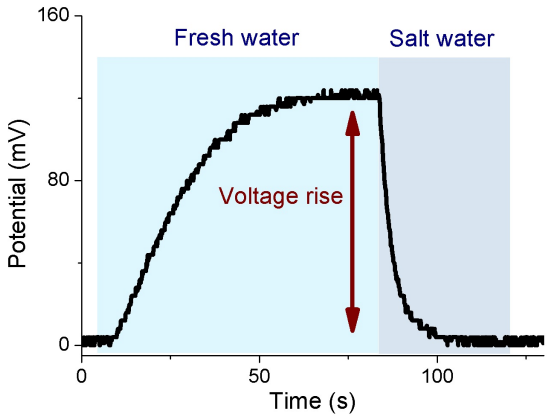

FIG. 6. Capmix cell potential evolution (OCV) as a function of time when fresh water and salt water are alternatively introduced.

Firstly, we studied the influence of real river waters from Gulf of Fonseca. Fig. 7 shows the OCV evolution when real river water and reference fresh water solutions are exchanged with reference salt water. Surprisingly, it is found that that the voltage rise is larger for the three real river waters, reaching a maximum of 250 mV for El Rebalse, which is indeed the one further from the coast. The reason for this result is probably that the samples were collected during the rainfall regime (October), and therefore, the salinity of the river water was less than the simulated one. This produces a voltage difference that almost doubles the reference potential measurement. The electrical conductivity data shown in Table I confirm this explanation.

TABLE I. Electrical conductivities of each of the measured river waters from the Gulf of Fonseca and fresh reference solution.

River Water	Conductivity
Rebalse	234 μS/cm
Amatillo	274 μS/cm
Pavana	570 μS/cm
Reference	2.19 mS/cm

Subsequently, the effect of real sea water in comparison with the simulated sea water was studied. In these measurements, the reference fresh water solution was used

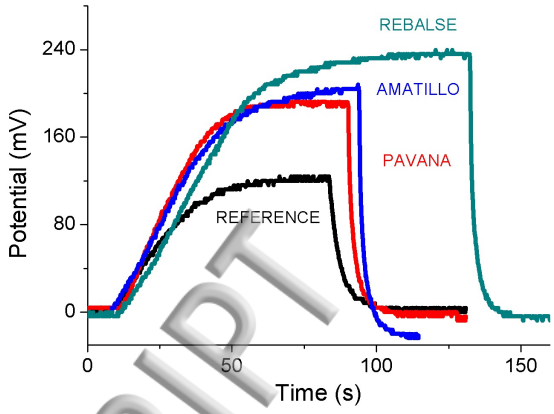

FIG. 7. Evolution of the cell potential as a function of time when fresh water from rivers in the Gulf of Fonseca (El Rebalse, Amatillo, Pavana) and reference fresh water solution are exchanged with salt water reference solution.

for exchanging in both cases. Fig. 8 shows the evolution of the cell potential. As it can be seen, there is a small decrease in the voltage rise from 120 mV to 110 mV when actual sea water is introduced. The reason for this measurable voltage rise decrease is likely related to the effect of multivalent ions which are present in real sea water[23,24]. Ions such as magnesium or calcium produce a decrease of the double layer expansion and, in addition, their larger size is responsible for the decrease of the stored charge at the electrodes. These two factors working together bring about a reduction of the voltage rise.

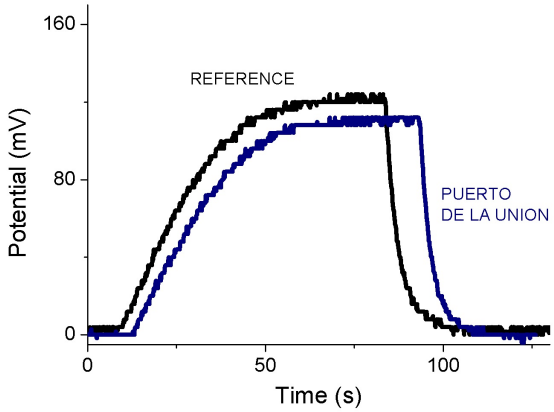

FIG. 8. Evolution of OCV versus time when salt water from Puerto de la Union and reference salt water solution are introduced. Fresh water is in all cases the 1 g/L NaCl reference solution.

A final comparison will be presented of the evolution of the OCV for realistic sea and river water solutions with

the simulated concentrations of sodium chloride. Fig. 9 shows that, as expected from results above discussed, the voltage rise is considerably improved by introducing river water from El Rebalse even when we use natural sea water from Puerto de la Union. Despite the presence of other ions, the use of unfiltered water and the possible presence of black water, we do not find a decrease of the voltage rise. Indeed, an important increase is found associated to the lower salinity of the natural river samples during the experimental period. Thus, it can be concluded that soft electrode capmix techniques will be highly favoured during the rainy season when much better results than those obtained with the laboratory reference are found.

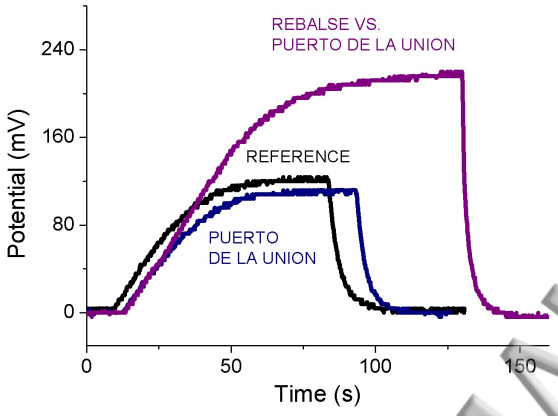

FIG. 9. Evolution of cell potential versus time when salt water from Puerto de la Union and reference salt water solution are introduced. Fresh water is in all cases the 1 g/L NaCl reference solution.

IV. CONCLUSIONS

The results of this research reveal the possibilities of blue energy extraction in the Central America context using the soft electrode technique, a novel capmix method that has been presented as a promising alternative due to its easy electrode preparation. Blue energy can become an economic and environmentally sustainable energy source, since it is based on natural mixing processes that occur in river mouths and estuaries, as presented in this work, and generates no CO_2 or any type of thermal contamination. Open circuit voltage measurements have been performed to study the maximum voltage rise between electrodes of polyelectrolyte-coated activated carbon film for real sea and river waters of the Gulf of Fonseca (El Salvador). This location has been selected as a region of high salinity water concentration and at the same time, a great abundance of rivers. After the performed experimental study, it can be concluded that even the presence of multivalent ions and dispersed pollutants (mineral particles, bacteria) does not significantly influence this capmix technique, capable of providing better results than those obtained with the reference solutions. The reason comes from the heavy rainy season when all samples were taken. This would lead to consider the high potential of this technique in the winter season in Central America.

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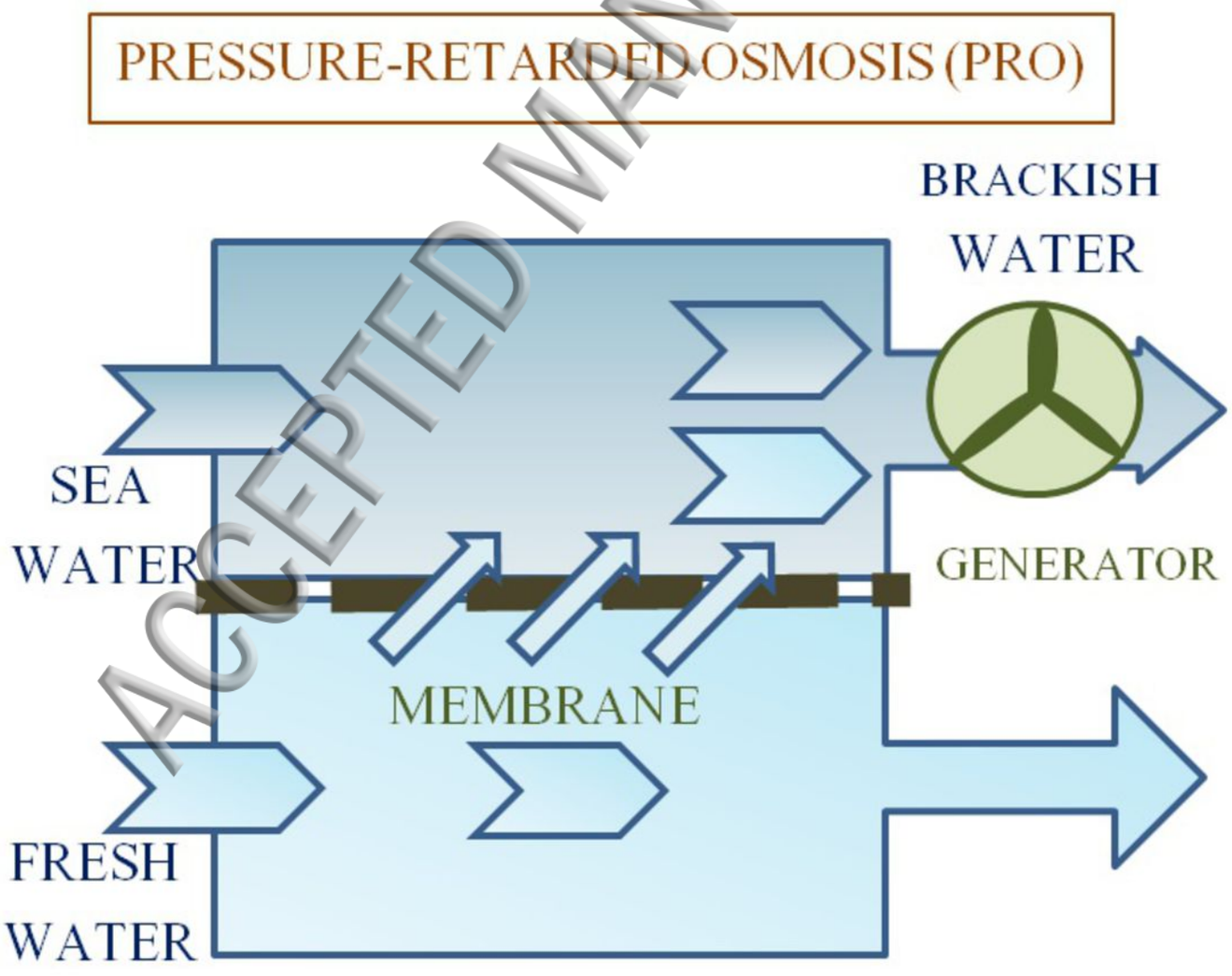

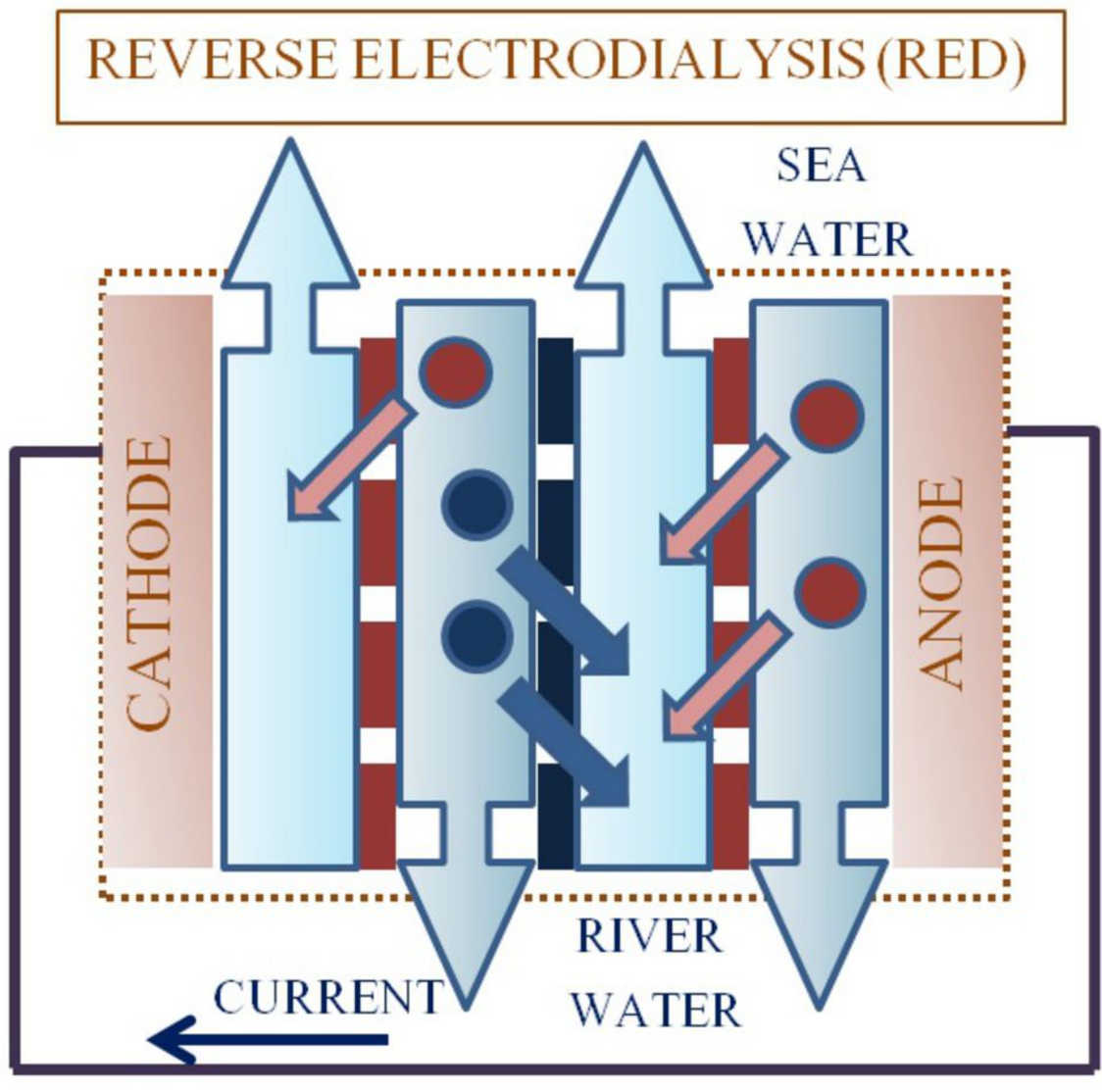

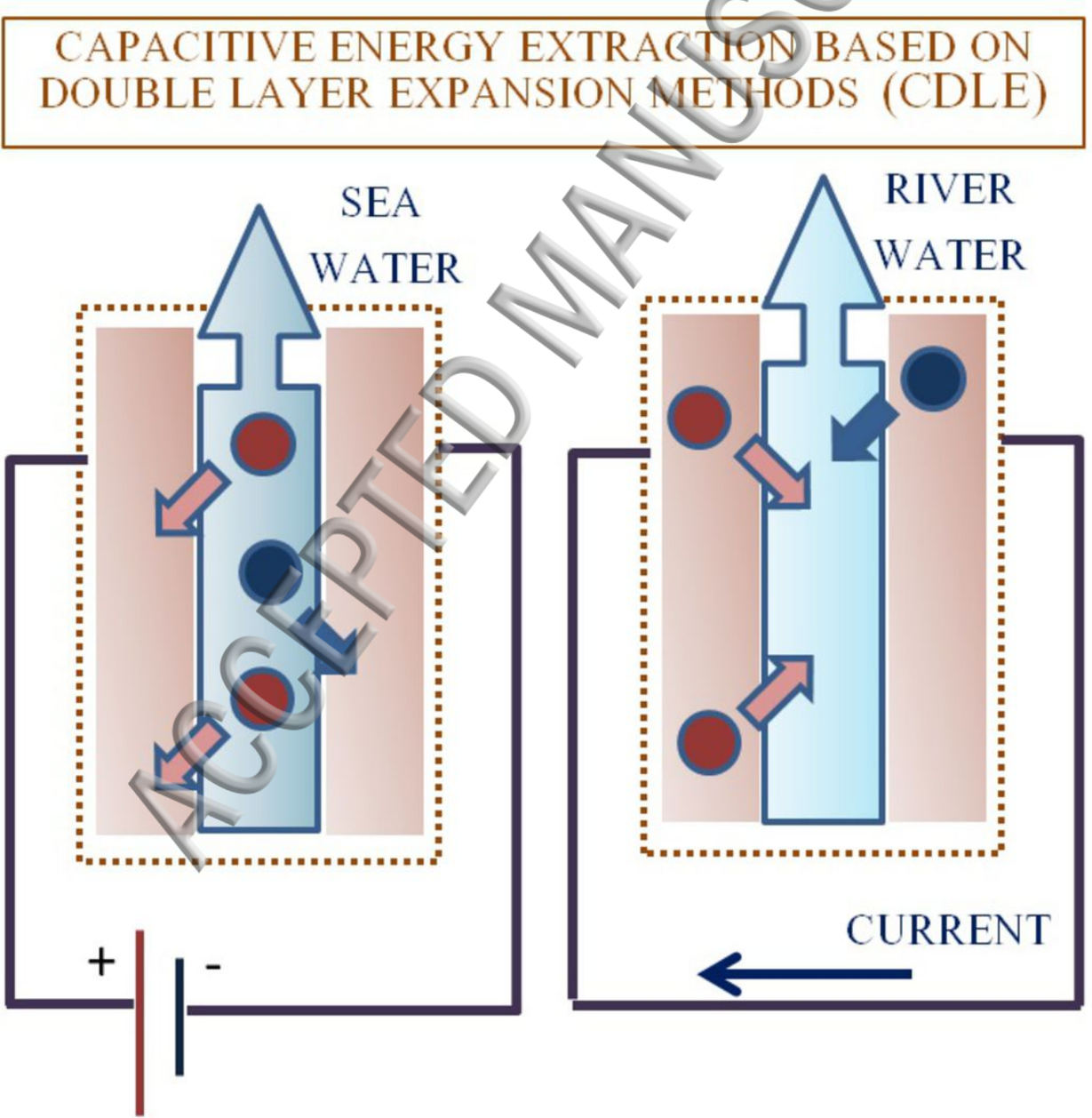

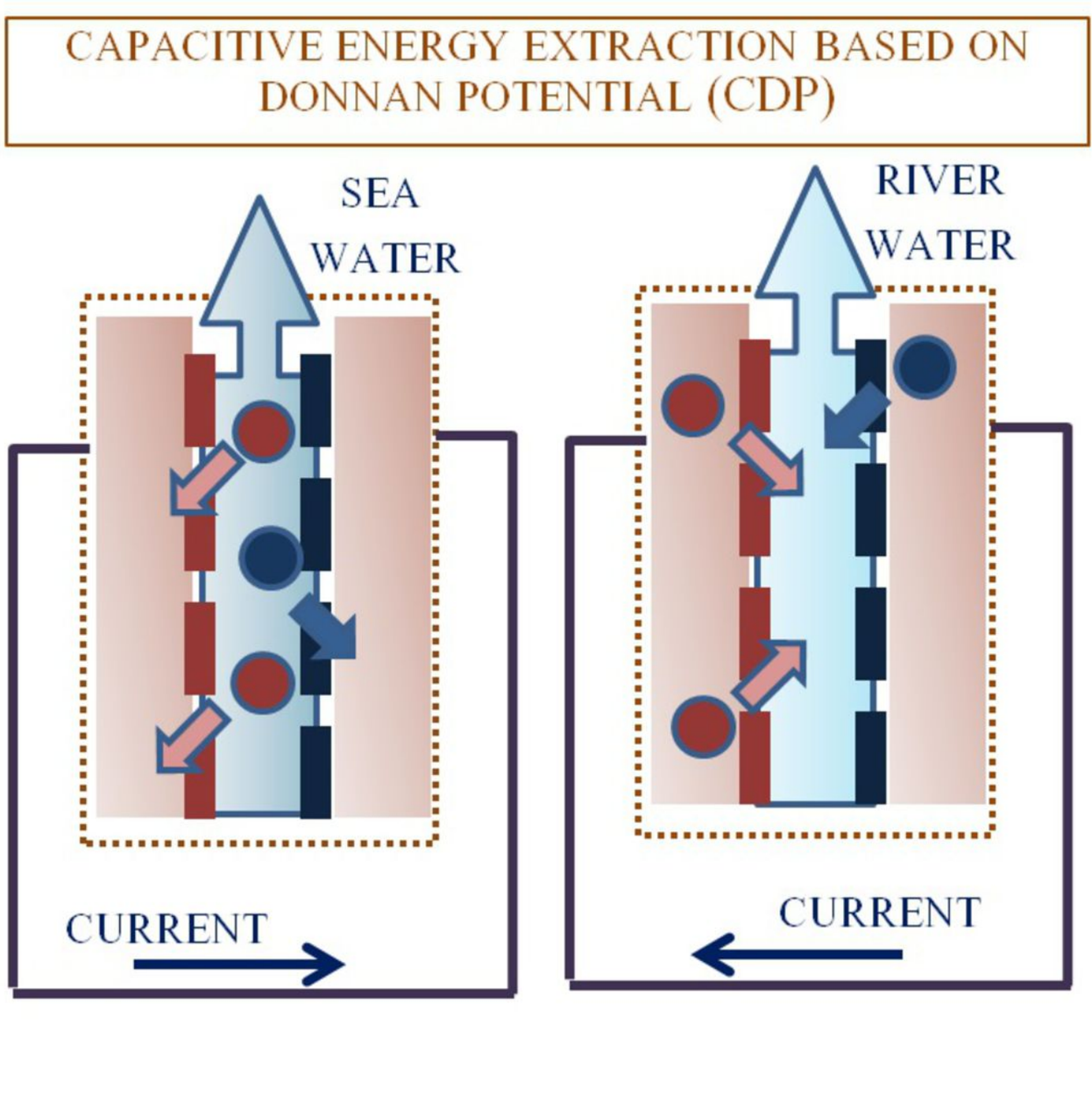

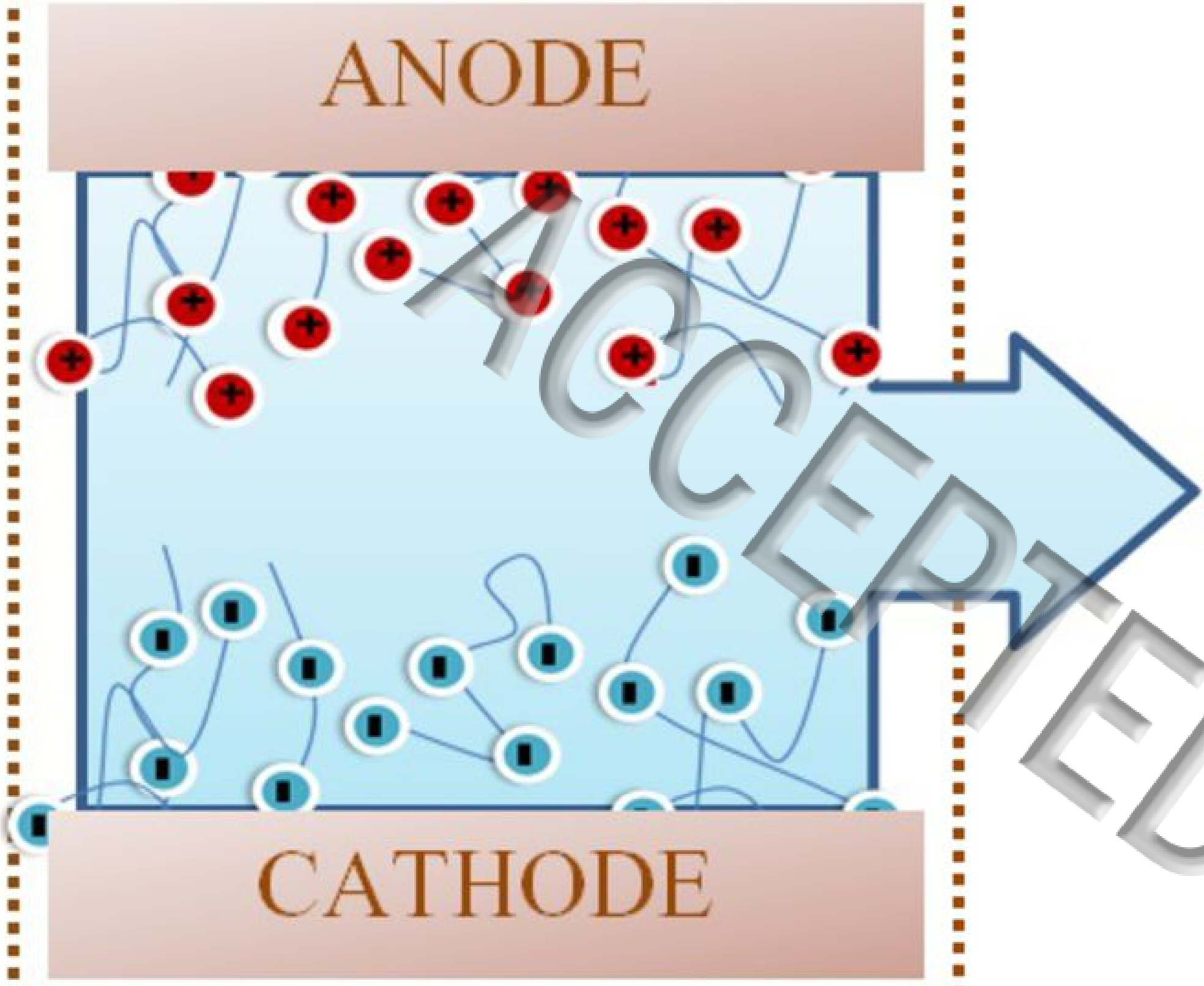
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