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# Stacking of capacitive cells for electrical energy production by salinity exchange

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## HIGHLIGHTS

- Several associations of individual Capmix cells are explored.
- In CDLE serial configuration, cells are partially short-circuited.
- The use of coated electrodes is preferred for series stacking.

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## ABSTRACT

In this paper we explore methods for stacking individual cells in order to increase the amount of energy that can be extracted from salinity gradient cycles (capmix methods). Each of the cells consists of a pair of parallel electrodes made of activated carbon particles, either bare or coated by a layer of polyelectrolyte. In these methods, energy is produced based on the modifications of the electrical double layer (EDL) structure in the pores of the carbon particles upon exchange of the salinity of the surrounding medium. In the case of the bare carbon particles, the electrodes are externally charged in presence of high-salt concentration, and discharged after exchanging the solution for a dilute one (sea-vs. river-water cycles). In a first stacking approach, we simply connect the electrodes side-by-side and only the outermost ones can be connected to the external source. Using a stack where potential and current between cells can be measured, it is shown that only the external electrodes seem to work, and it is suggested that this is a consequence of internal short-circuit currents between oppositely charged electrodes of different cells through the electrolyte. In contrast, the side-by-side configuration is operational if coated electrodes are used.

## 1. Introduction

Although still not fully explored, the possibility of obtaining clean electrical energy by the so-called capmix methods (belonging to a larger group of methods, typically known as *blue energy* techniques), based on changing the salinity of solutions in contact with large surface area electrodes, appears as a promising member of the list of renewable and clean energy sources [1–10]. We focus on two of the capmix technologies, in which the electrodes are either externally charged before exchanging the solutions (CDLE or Capacitive energy production by Double Layer Expansion), or spontaneously charged by coating them with either ion exchange membranes (CDP or Capacitive energy extraction based on Donnan Potential, [11]) or polyelectrolytes (SE or soft electrodes, [6]).

In CDLE, a pair of porous (typically activated carbon) electrodes are immersed in a high-salt (sea water, say) solution, and externally charged by connecting them to a power source. At constant charge (open circuit), low-salt solution (river water, for instance) substitutes the sea water, producing an electrical double layer (EDL) expansion, and subsequently an increase in potential. The energy produced comes from the recovering of part of the charge externally provided, but at that increased voltage. In contrast, the CDP technique is based on the spontaneous generation of a Donnan potential difference, brought about by the use of ion-specific membranes (cationic and anionic in the opposed electrodes). Finally, in SE, the role of the membranes is played by the coating of

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the electrodes with a layer of cationic and anionic polyelectrolytes, respectively.

Not all these methods are capable of producing the same amount of energy or power. Typically, CDLE yields 300 μJ/cycle, while with SE one obtains 15 mJ/cycle and the amount jumps to 20 mJ/cycle in CDP. In terms of power, the figures are 10–20 mW/m$^2$ (CDLE), 30 mW/m$^2$ (SE) and 100–300 mW/m$^2$ (CDP). Considering specifically CDLE, theories of EDL capacitance [12,13] predict that the voltage rise when salty and fresh water solutions are exchanged is about 80 mV on each electrode, while the surface charge density typically changes by 0.05 C/m$^2$. This means that in a complete cycle the energy obtained should be around 8 mJ per square meter of EDL. Furthermore, taking into account that the experiments are carried out with activated carbon or similar material with a specific surface area of ~1000 m$^2$/g or more, the energy that might be made available could amount to 16 J/cycle with just 1 g of carbon per electrode. A power density estimation can be given: assuming that the mass of carbon is distributed on an area of 20 cm$^2$ (this would be the apparent electrode area), and that the cycle duration is 100 s, the power available would be 8 W/m$^2$, if the efficiency is 10% [14].

These power densities can be compared here to those obtained in other blue-energy devices, based on different principles, but always taking advantage of salinity gradients. For example, in reverse electrodialysis (RED), salty and fresh waters are made to flow in alternate compartments separated by anionic and cationic exchange membranes. The best technology available yields 2.2 W/m$^2$ (1.2 W/m$^2$ if account is taken of the pumping energy needs), although simulations predict even higher values, approaching 20 mW/m$^2$, upon design improvements [15,16].

Recently, Yip and Elimelech [17] compared the efficiencies and power densities achievable with RED and the other widely studied technique based on salinity gradient, namely, PRO, or *pressure-retarded osmosis*. In this, the difference between the osmotic pressures of salt and fresh waters is used to build up pressure in the high-concentration container using a semipermeable membrane separating both solutions. Useful work is produced by releasing the pressure through an electric turbine. These authors calculated the power density of the RED technique based on the product of the current per unit membrane area times the potential difference across the external load. In the case of PRO, the power produced per unit area of membrane is calculated simply as the product of the pressure difference and the solution flow rate. Typical values for PRO are in the range 3–9 W/m$^2$ for sea water-river water or brine-waste water salinity gradients. Smaller values (around 1 W/m$^2$) are also predicted in this work for RED. Regarding efficiency, the method used for its calculation involves comparison of the actual useful work with the Gibbs free energy of mixing known proportions of solutions with different concentrations [18–20]. Typical results indicate efficiencies in the order of 54% (38%) for PRO (RED) when combining 600 mM–1.5 mM NaCl solutions.

In contrast, the predicted amounts of energy for CDLE are way larger than those experimentally achievable. The reason for this may be the existence of charge leakage [21] by progressive discharge of the EDL, incomplete wetting of the available pore area [22], hydrophobicity or oxidation of the activated carbon, etc. Whatever the reason, it is clear that some method must envisaged in order to increase the amount of energy and power available, if the technique should become competitive at some time.

Furthermore, in order to implement this technique in an electronic circuit, higher voltages are required, more than 1 V being preferred. This goal can be achieved by amplifying the output signal, which runs against the efficiency, or improving the cell design. In this work, we propose to increase the voltage output by associating several individual cells, as previously done with other capmix devices [23–26].

In this contribution we show some possible ways to do this, both in CDLE and in polyelectrolyte-coated electrodes. The aim of this work is to find the optimum configuration of the multi-electrode setup for maximizing the energy and power outputs. Side-to-side (serial) configurations will be considered, and the results will be compared to theoretical predictions based on models for EDL expansion and Donnan potential generation in carbon electrodes.

## 2. Experimental

### 2.1. Materials

Norit DLC Super 30 activated carbon particles (Norit Nederland B.V., The Netherlands) mixed with poly(vinylidene-fluoride) (PVDF) as binder are deposited on a double-sided graphite current collector, 2 mm thick (Mersen, Spain). One side is used as the electrical contact and the other is painted with a thin layer of activated carbon particles with a layer thickness of about 250 μm. Facing electrodes are separated from their neighbors by a 500 μm plastic spacer. Sea and river waters are simulated with NaCl (Scharlau, Germany) solutions in deionized water (Milli-Q Academic, Millipore, France), with respective concentrations 500 mM and 20 mM.

In the CDLE technique the electrodes are used without treatment, while in SE the activated carbon films are coated with the anionic polyelectrolyte poly(sodium 4-styrenesulfonate) or PSS, with a typical molecular weight of $M_w \approx 7 \times 10^4$, or the cationic one, poly(diallyldimethyl ammonium chloride, PDADMAC), with $M_w \approx 1 - 2 \times 10^5$, both from Sigma Aldrich (Spain). The coating was produced by keeping the carbon-coated graphite films (typically 2 × 2 cm$^2$) in contact with 50 mL solutions of the respective polyelectrolyte, with concentration 60 mM on a monomer basis. After 24 h contact, the films were thoroughly rinsed with deionized water.

### 2.2. Stacks design

Fig. 1 shows a scheme of the individual cell association designed in stack#1, based on our optimal device, described in Refs. [22,26]. As shown in Fig. 1 (center), the cell consists of several units. In the case of two and three units, the central films were obtained by coating both sides of the graphite substrate with the activated carbon layer. The same kind of association was used in the SE technique, although in that case the central elements were PSS/graphite/PDADMAC.

With the aim of analyzing the behavior of every unit in the stack, we designed the stack#2 (Fig. 2). In this case, the carbon films were cut into 30 × 30 mm$^2$ pieces and placed in contact with square graphite collectors. This stack is basically the same configuration as stack#1, but individual determinations are possible. All the electrodes are in contact with the same solution bath, but now adjacent cells are externally connected.

## 3. Results and discussion

### 3.1. Cell stacking in CDLE

We will consider the series association shown in Fig 1 (center). It might be expected that by associating the electrodes back-to-back, the voltage rise linked to each pair would be multiplied by the number of cells. If the internal resistance per pair does not change substantially, then the current will be comparable to that of a single cell and as a result, the power would be increased by a factor equal to the number of individual cells. The comparison between voltages and currents oscillations along the cycles, obtained with one, two