



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.

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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 $\mu\text{J}/\text{cycle}$, 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 $\sim 1000 \text{ m}^2/\text{g}$ 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 $2 \times 2 \text{ cm}^2$) 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 $30 \times 30 \text{ mm}^2$ 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

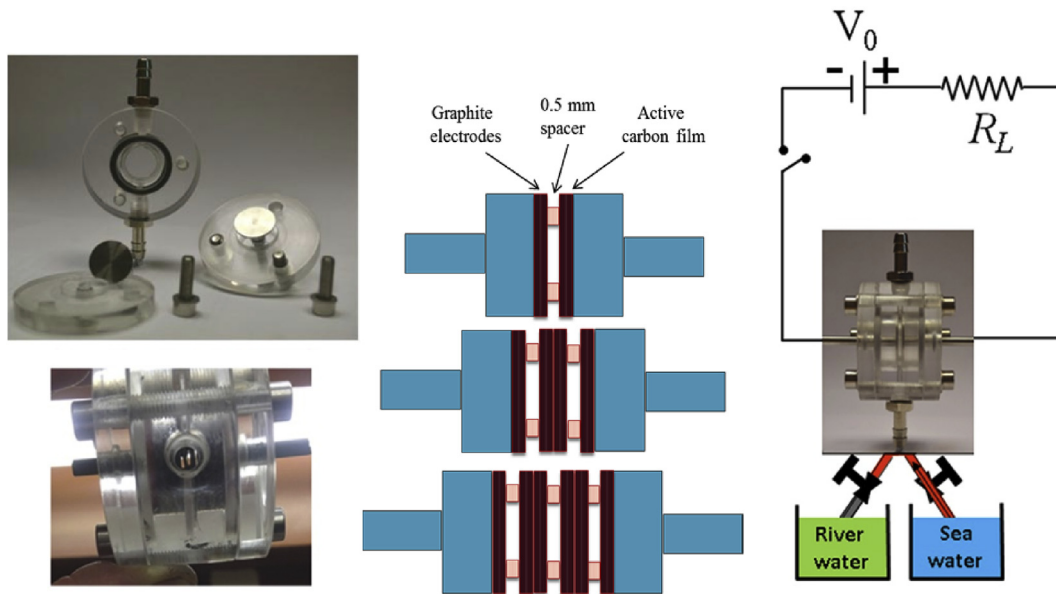


Fig. 1. (Left) Photo of the acrylic individual cell. (Center) Sketch of the association of individual cells used in stack#1. (Right) Electrical and salt reservoir connections; R_L is the load resistor and V_0 is the charging voltage source.

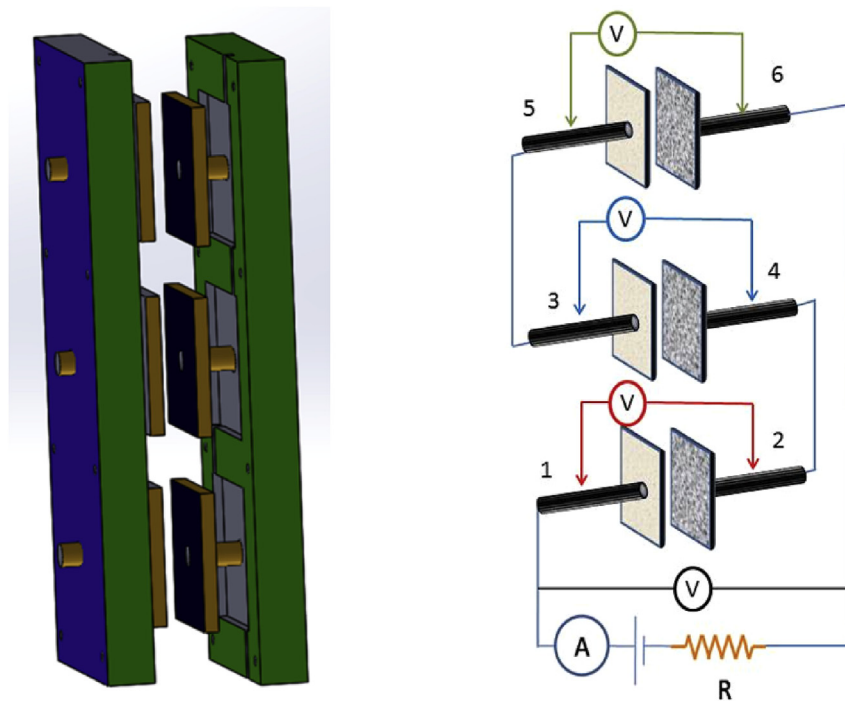


Fig. 2. (Left) Sketch of stack#2 configuration. (Right) Electrical connection in series of the sealed stack.

and three cells is presented in Fig. 3. The cycles start with the charging process of the cell. Negative currents in this Figure correspond to this process, and positive ones indicate charge extracted from the system (discharging of the cell).

We observe that the total voltage used for charging was roughly three times larger than the one needed in the simple cell setup. The average voltage rise when fresh water enters the stack was about 29 mV, 44 mV, and 65 mV for one, two, and three cells, respectively. Although the voltage elevation increases with the number of cells, it is not strictly proportional to this number. In addition, the

charging and discharging currents are very similar in all cases, indicating that even if the charging voltage is three times larger, so is the internal resistance. Hence, both sets of data taken simultaneously suggest that the proposed stack association produces an amount of energy which does not increase as much as expected.

Using the data in Fig. 3, we can calculate the energy per cycle in each of the associations, including the single-cell device. Thus, the CDLE stack produces an average of 0.21, 0.78, and 0.76 mJ per cycle, for one, two and three electrode pairs, respectively. Considering the electrode area ($3.14 \times 10^{-4} \text{ m}^2$ each), these values

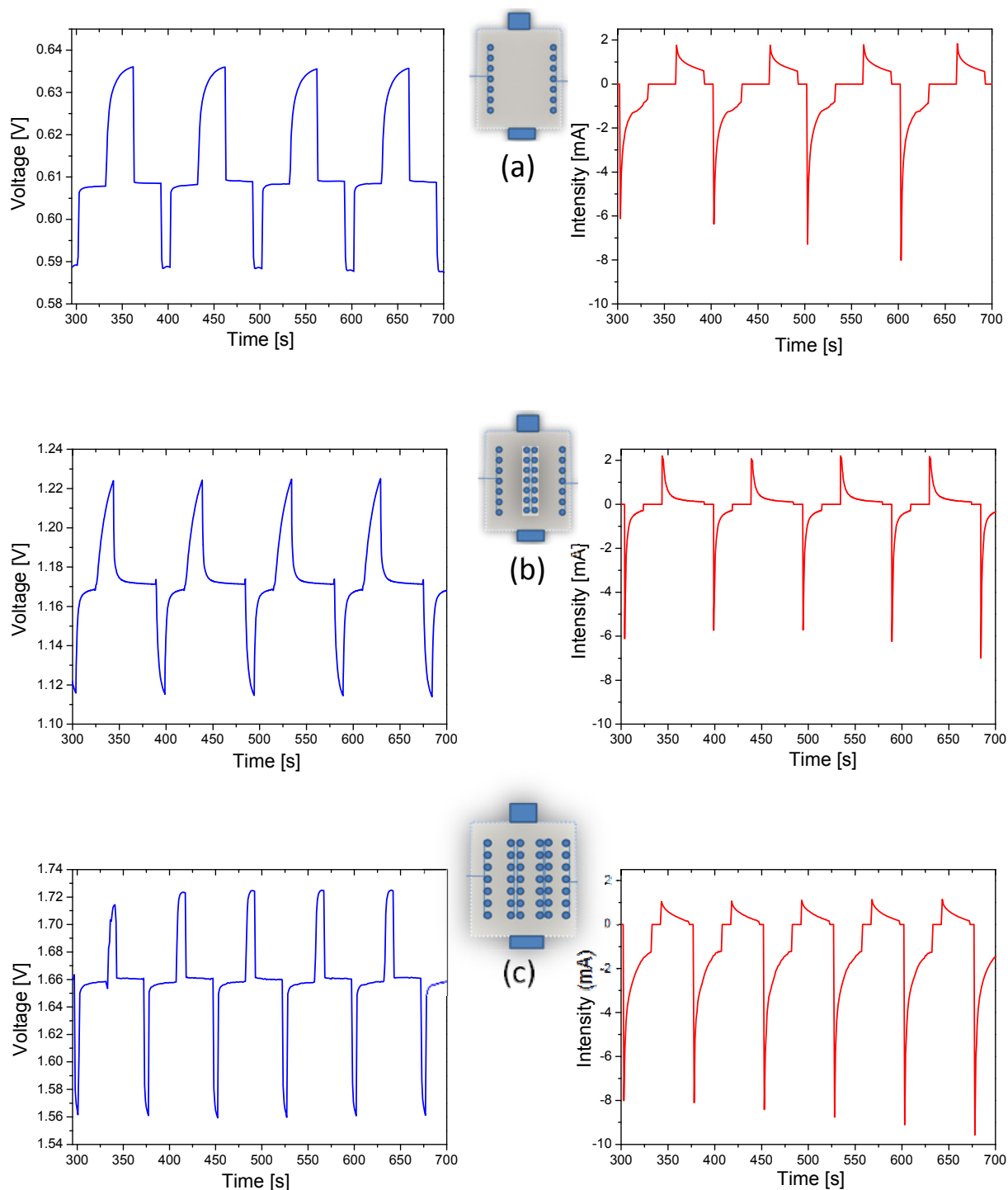


Fig. 3. Voltage and current cycles in the CDLE experiments with one (a), two (b) and three (c) cells connected in series. The charging voltages were 0.605 V (a), 1.17 V (b) and 1.66 V (c).

correspond to 330, 620, and 400 mJ per m^2 of apparent electrode area. In order to estimate the efficiency of the technique, several possibilities do exist [27]. In this contribution, we choose one based on the comparison between the area of the experimental cycle and the theoretical predictions [12] based on a cycle where the charge transferred in the process equals the experimental one. Fig. 4 shows the details: the predicted voltage jump and charge transferred (per unit area of pore) are, respectively, 160 mV and 70 mC/m^2 , if the electrode voltage is 300 mV, and the exchanging solutions are 500

and 20 mM NaCl. For these calculations, the carbon film is simulated as a network of cylindrical pores 5 nm in radius. With these data, the energy that could be theoretically obtained amounts to 5.6 mJ per m^2 of pore area. Integration of the current vs. time curves in Fig. 3 allows us to determine the exchanged charge, namely, 27.2 mC for a single cell. This means that the electrode area effectively participating in the capmix process is $(27.2 \text{ mC})/(70 \text{ mC}/\text{m}^2)$, or 0.39 m^2 . This is approximately 1% of the total pore area in a carbon film, considering the specific surface area of Voltea carbon

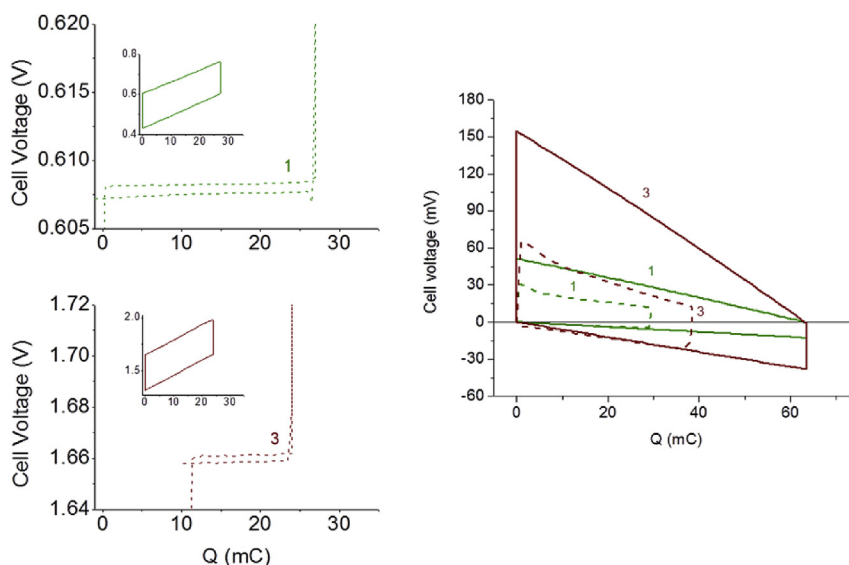


Fig. 4. Left: CDLE cycles for one and three cells. Inset: Theoretical calculations for the same charging voltage and amount of charge transferred. Right: Energy cycles for coated (SE) electrodes. Theoretical (solid lines) and experimental (dashed lines) results. The number of stacked cells is indicated.

(959 m²/g) and the amount of carbon per electrode (0.038 g). This reduced use of the available carbon pore surface is quite common in capmix systems: the exchange of solutions does not reach the whole pore surfaces to the same extent. This is confirmed in numerical simulations by Rica et al. [28]. As Fig. 4 shows, the area of the experimental cycle is smaller than that of the theoretical one: the voltage drop in internal and load resistances is not taken into account in the model, and furthermore, the voltage rise is also lower than predicted, due to unavoidable leakage. The amount of energy that might be obtained from one cycle would be 5.6 mJ/m² × 0.39 m², or 2.1 mJ. Referred to the apparent electrode area (discs of 1 cm in radius), the result is 6.7 J/m². Since our experimental data is 0.333 J/m², we can conclude that the device allows to obtain 5% of the energy available for one cell. The calculation for three cells in series is also shown in Fig. 4: the prediction in this case is 4.3 J/m², and our efficiency would be around 10%. In this calculation, the work required for the initial charging of the electrodes is not included. It can be estimated to be on the order of 17 J, although the full charging must be performed only once during operation, and hence this requirement of further energy (when divided by the number of cycles) can be made negligible. In addition, in our device we do not use pumps, but valves, and the solutions are fed by gravity. The power required for opening the valves is 12 W, so that a completely autonomous system would require a significant up-scaling.

In order to find an explanation for this behavior, stack#2 (Fig. 2) appeared useful, since it allows for the separate connection of each individual cell to the external circuit. Although this might suppose a larger internal resistance, and it is certainly less compact than stack#1, it offers access to individual measurements. As an example, Fig. 5 shows the voltage of each electrode pair (numbered as in Fig. 2) and the total current during successive cycles, after charging with 1.48 V between the outermost electrodes.

It must be noted that the base voltages of each pair are different (Fig. 5 left), and do not correspond to the expected value, namely, one third of the overall applied voltage difference. This can be understood by considering the simulation (using LTspice IV, Linear Technology, USA) of the process of charging a series association of capacitors in two cases: the ideal one where conductive connections do only exist between adjacent plates (Fig. 6 top) and one in

which cells are further connected through external resistors, simulating the conducting path established by the electrolyte solution (Fig. 6 bottom). In the latter case, the stationary voltage of every cell is in good agreement with the simulation results. This calculation indicates that the effect of the conduction between plates of different cells leaves the inner cell (not directly connected to the external circuit) inoperative. Hence, only the capacitors in contact with the charging source contribute to the voltage rise, while the latter is negligible for the internal cell, effectively charged with a low voltage. This limitation appears inherent to the series connection in the CDLE technique.

The fact that the charging voltage is different for each pair has important consequences on the CDLE cycles. As shown in Refs. [5,22], the voltage rise associated to the exchange of salty for fresh water is maximum at intermediate charging voltages. As illustrated in Fig. 5, this is precisely what we find: the voltage rises are as indicated in Table 1, and they decrease when the effective charging voltage is above 300 mV, roughly, a confirmation that an optimum working voltage exists for CDLE, and that even in stacks, any sub-cell being charged above or below that optimum value will be working out of the best regime.

Both results, namely, the lack of activity in the inner cell and the deviation from the optimum conditions in each of them, are very significant for the design of practical setups based on the CDLE principle: although association in series might increase the potential jumps, such an increase is in reality very limited, and does not compensate for the rise in internal resistance.

3.2. Association of polyelectrolyte-coated electrodes

One way of improving on the CDLE method, as already mentioned, is based on using activated carbon films coated with polyelectrolyte layers, with either negative (PSS) or positive (PDACMAC) distributed charges. The electrodes are in this case spontaneously charged by the Donnan potential originated in each layer [6]. Hence, no external charging is necessary. Note that in CDLE energy can be extracted only in the discharging step, while in SE energy can in principle be extracted after every exchange of water. No external source is necessary and the method will be free of the limitations of CDLE when stacking several cells.

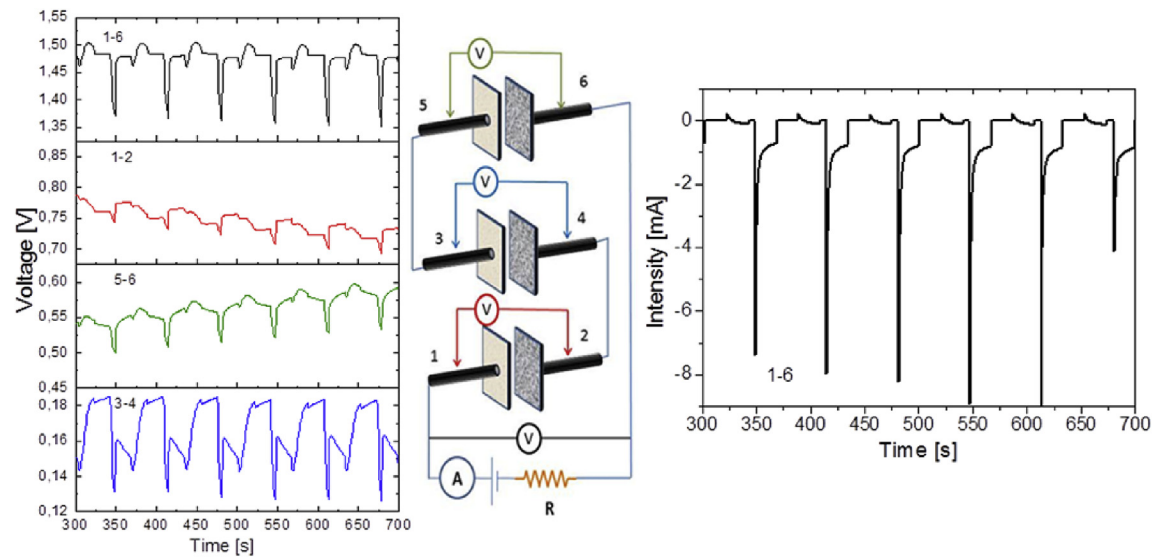


Fig. 5. Voltage (left) and current (right) oscillations during the Capmix cycles. The left panel shows the oscillations of the voltage difference between the indicated electrode pairs.

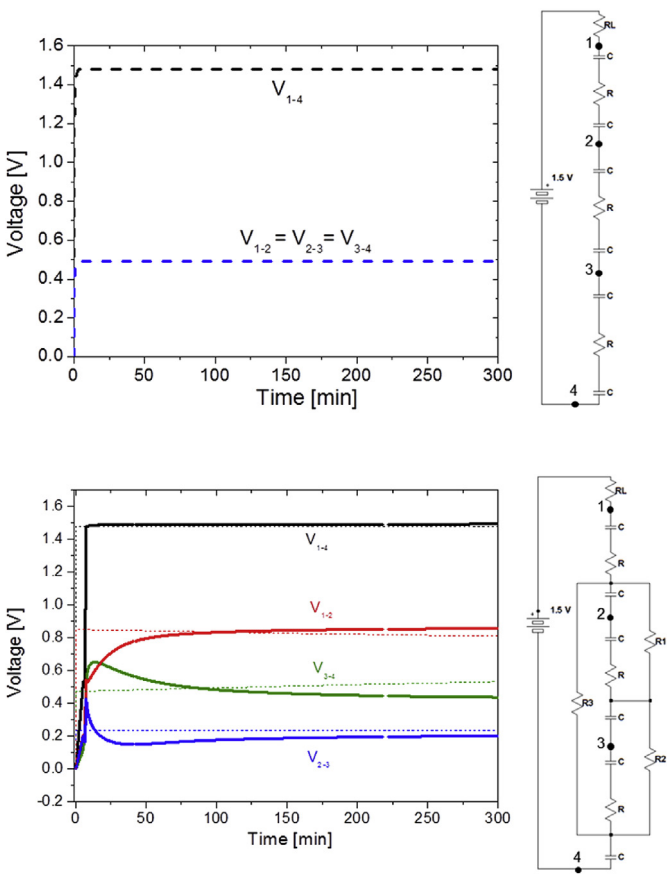


Fig. 6. Time evolution of the voltage of individual capacitors in a series association. Top: Conductive connections exist only between neighbor plates. Bottom: experimental charging data in stack#2 (solid lines), and simulations (dotted lines) when additional connections are established through external resistors. The parameters used for the simulation are: $C = 1 \text{ F}$; $R_L = 5 \text{ }\Omega$; $R = 100 \text{ }\Omega$; $R_1 = 50 \text{ }\Omega$; $R_2 = 200 \text{ }\Omega$; $R_3 = 500 \text{ }\Omega$.

In Fig. 7 we show the voltage of the stack#1 with up to three pairs of films (PSS-PDADMAC//PSS-PDADMAC//PSS-PDADMAC)

Table 1
Charging and rise voltages for the different electrode pairs connected in series as in Fig. 2.

Pair	Charging voltage (mV)	Voltage rise (mV)
1–2	0.761	–5
3–4	0.145	+30
5–6	0.558	+15
1–6	1.460	+40

upon successive exchanges of salty for fresh water and viceversa. As expected, the cell potential (a result of the difference between the respective Donnan and EDL potentials) increases when fresh water enters the inter-electrode spacing and decreases when it is salty water that feeds in. Additionally, it increases with the number of cells in the stack.

From the practical application point of view, it is also important to consider the behavior of the stack in closed circuit operation, when it is maintained in connection with the external load resistor all times. The result in this case is most promising, as we can see in the representation of Fig. 8. The increase in power available when the electrodes are associated in series is a certainly significant result, ranging from 30 mW/m² for one pair of electrodes, to 77 mW/m² in the case of using three pairs of treated activated carbon films. This positive outcome comes from the fact that the individual capacitors are spontaneously and independently charged by the presence of the polyelectrolyte coating, without the need of connection to an external source and the subsequent coupled charging process.

It may be of interest to analyze, as was done before in the analysis of the CDLE stack, the efficiency of the SE cells by comparing the cycles obtained with those predicted using a model for polyelectrolyte-coated electrodes [6]. This is done in Fig. 4: as in the CDLE case, we start from the experimental data of charge transfer, and use the calculations described in Ref. [6]. Using electrophoretic mobility data we could estimate the volume charge density of the polyelectrolyte coatings ($\pm 6 \times 10^6 \text{ C/m}^3$), and the electrokinetic theory for soft particles was used for predicting the voltage-charge profiles in the coated electrodes. The results in Fig. 4 confirm that our experimental data in SE cells approach the theoretical predictions, so that the efficiency, evaluated as the ratio

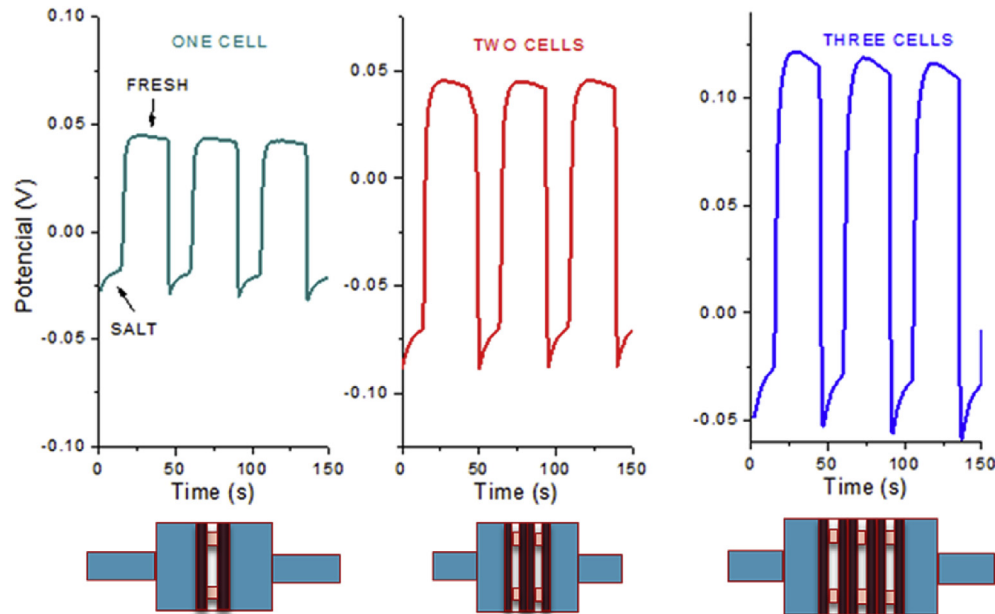


Fig. 7. Open circuit voltage for one, two, and three stacked cells (stack #1, Fig. 1) consisting of PSS/PDADMAC coated pairs of electrodes, when salty and fresh solutions are exchanged.

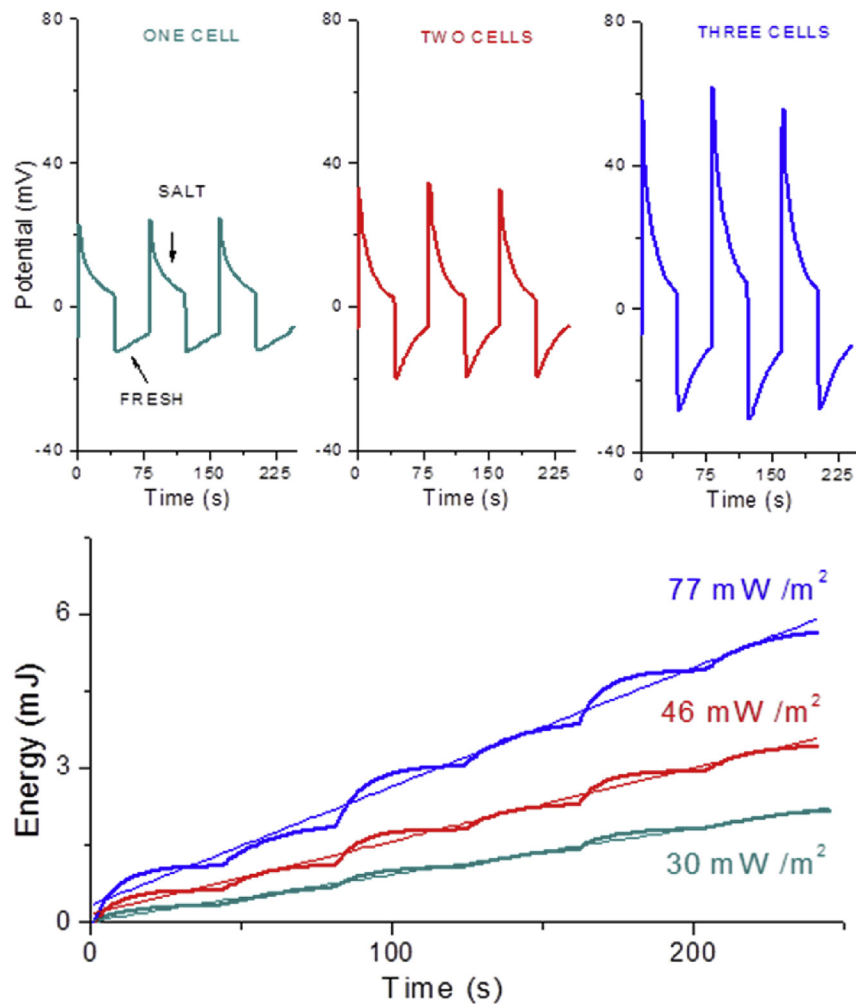


Fig. 8. Top: cell potential cycles in one, two and three cell stacks in closed circuit operation with a 10 Ω load. Bottom: energy vs. time, and average power in each case.

between the areas of the measured and predicted cycles amounts to 54% (single cell), and 40% (three cells connected). It can be suggested that the SE technique is very suited to series association for increasing the output power, without reducing efficiency significantly.

4. Conclusions

Searching for increased energy and power production in capmix (capacitive mixing) techniques, we investigate the possibility of associating individual cells (pairs of porous electrodes) in series. The challenges for the stacking of cells can be summarized as follows:

- Ensuring that all available area exchanges the solutions when required in CDLE. An optimal hydrodynamic design will probably be necessary. Perhaps, two continuous films of active carbon should be preferred over the parallel stacking. This is well known in the supercapacitor technology.
- Avoiding the fluid connections between the individual cells, to reduce charge losses.
- The polyelectrolyte-coated electrodes seem to be the preferred option, since no charging is necessary, and all parts of the cycles produce useful energy.

Using the CDLE method, it is found that the voltage rise when salt water is substituted by fresh water is roughly a multiple of the rises of individual cells, while the current is the same in all cases. An analysis performed on individual cells demonstrates that the conductive connection between non-adjacent units due to the permeating electrolyte solution leaves only the outermost cells as actually working ones. In contrast, the series association appears very advisable when the technique used is based on poly(-electrolyte) coated (or spontaneously charged) electrodes. In such a case, the open circuit voltage effectively increases with the number of cells connected, and, most important, the power produced also increases when a closed circuit configuration, with a load resistor always present, is employed.

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