

# Optimization of Energy Harvesting in CapMix Cells

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**Abstract**—Blue energy has revealed as an alternative to other widely used sources of renewable energy. This power source derived from the process of mixing sea and river water still remains to be fully developed. Research on the materials used to produce the cells that capture this energy is one of the topics that will definitely contribute to the development of this technology. And just as important, if not more, is the research related to the systems that must be used to extract the stored energy.

This paper shows the influence of the porous carbon used to manufacture the cells and provides insight into the selection of the optimum current that must be used to extract the energy from the cell. These contributions are supported by both simulations and experimental results.

**Keywords**—blue energy, CapMix, discharge current.

## I. INTRODUCTION (HEADING 1)

The current energy crisis is pushing even harder towards the use of renewable energies [1]. This decision is no longer based solely on an environmental issue (reduction of greenhouse gases in the atmosphere, especially carbon dioxide), but on economic reasons as well. Thus, additionally to *classical* sources of renewable energy (solar, both thermal and photovoltaic, wind, hydroelectric, ocean, biomass), other forms of renewable energy must be explored. One alternative is the so-called blue energy.

Blue energy is based on the free energy produced when water with different salt concentrations mix (which is something that is continuously happening at the mouth of rivers) [2]. The goal is to harvest this salinity gradient energy as efficiently as possible and then inject it into a storage

element or directly into the grid. Different methods are being explored to achieve this objective (mainly Pressure Retarded Osmosis and Reverse Electrodialysis), but for the moment they are only available at a laboratory scale [3-5]. An alternative to these methods is using the CapMix (Capacitive Mixing) technique, which allows the electrical energy to be extracted with no need of turbines, heat engines or other electromechanical converters. CapMix makes use of the potential difference that appears in a cell formed by two electrodes when the ions of the water solution flowing through the cell are adsorbed by the electrodes thanks to the inclusion of ion exchange membranes [6].

The operating principle of the CapMix cell considered is based on the Donnan potential (Capacitive Donnan Potential), as illustrated in Fig. 1. When salt water flows through the cell, the exchange membranes cause the ions in the solution to diffuse to the electrodes: anions are adsorbed by one of the electrodes and cations are adsorbed by the other one. This produces a voltage difference that would make electrons flow from one electrode to the other if a load were connected between them, thus discharging the cell. If a dilute solution (such as river water) flows now through the cell, the ions previously deposited on the electrodes will be diffused through the ion-selective membranes into the solution, making the cell be negatively charged. In this case, electrons would circulate in the opposite direction if an external load were connected. Thus, by alternating the flow of freshwater and saltwater in the spacer channel, continuous energy production is generated as illustrated in Fig. 2.

This procedure has already been presented in several works that demonstrate that CapMix technology is suitable to

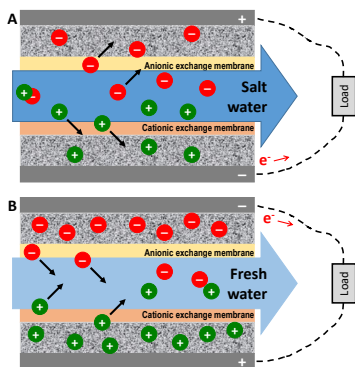


Fig. 1. Schematic representation of ion flow in a CapMix cell.

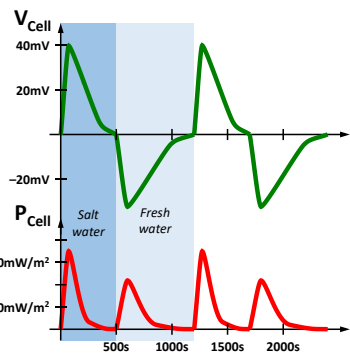


Fig. 2. Cell voltage and power in two subsequent cycles.

obtain energy from this salinity gradient [6-9]. However, the problem of extracting that energy from the cell in an efficient way seems to have been overlooked for the moment. This paper aims to offer some insight into that topic.

The organization of this paper starts with a description of the cells to use with CapMix techniques and the model considered throughout the work. Section 3 describes the electrodes used to build the cell and the parameters that may have an influence in their performance. Section 4 shows how to measure the electrical parameters of the cell. Section 5 analyses the optimum current value to be used when extracting the energy from the CapMix cell. Section 6 shows some results obtained with a preliminary prototype, and Section 7 contains the conclusions of this paper.

## II. STRUCTURE OF THE CAPMIX CELLS

As indicated above, a basic CapMix cell is formed by a couple of electrodes between which water flows. These electrodes are covered by ion exchange membranes that allow cations to be diffused to one of them and anions to the other one. Fig. 3 represents one such basic CapMix cell.

By alternating the flow of salt and fresh water through the cell, a voltage around  $\pm 100\text{mV}$  can be measured between the electrodes [6-9]. Typically, several electrodes must be connected in series as shown in Fig. 4 to obtain higher cell voltages that are more suitable to work with.

One of the most important part of the CapMix cells is the electrodes. As well as providing the electrical contact of the cell, the electrodes are in charge of adsorbing the ions. Therefore, they must exhibit two main features: they must be capable of adsorbing as many ions as possible and they should not result in a high series resistance of the cell.

Ion adsorption is achieved by screen printing a layer of porous carbon on a substrate that performs as current collector. This substrate must be made of a material that will not rust; note that the whole cell will be continuously operating in the presence of water. Also, it must have as low resistance as possible. The first choice was using titanium layers, 0.5-mm thick on which the carbon would be screen printed. These collectors were tested with different amounts and qualities of carbon. The tests carried always resulted in a series resistance close to  $1\Omega$ , too high to be just the resistance of the electrodes (with no membranes or spacers). It was concluded that the carbon did not attach conveniently to the titanium, thus resulting in a poor electrical contact.

Aiming to reduce the resistance introduced by the current collector, the titanium was replaced by graphite. Although the resistivity of graphite is higher than that of titanium, the

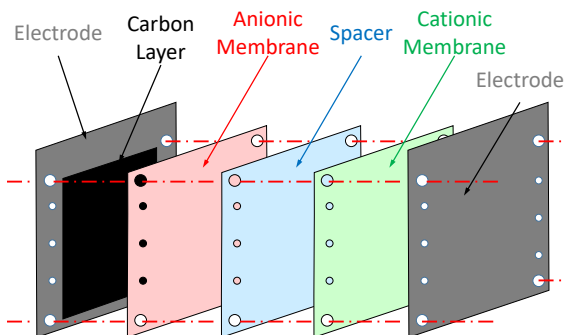


Fig. 3. Components of a basic CapMix cell.

porous carbon screen-printed on top adheres to graphite more easily. This compensates for the increase of the resistivity of the material and results in a lower overall resistance of the electrode as shown in Table I.

TABLE I. ELECTRODE SERIES RESISTANCE

	Inconel (0.5mm-thick)	Titanium (0.5mm-thick)	Graphite (2.0mm-thick)
$R_s$	$2\ \Omega$	$1\ \Omega$	$0.1\ \Omega$

The substrate used for the current collectors of the cells was thus chosen to be isostatic graphite (quality 1940), 2.0-mm thick manufactured by Mersen.

As far as the porous carbon is concerned, its properties and dimensions do highly influence the performance of the cell as a whole. On the one hand, the larger the amount of this material, the larger the number of ions that can be captured. On the other hand, the thicker the layer of carbon, the higher the series resistance of the cell. Therefore, electrodes with large carbon layers will be beneficial, but the thickness of this layer must be studied so that the increase in series resistance can still be compensated by the capability to adsorb ions. The type of carbon and the type and amount of binder used also determine the performance of the electrodes. After several tests carried out at INCAR-CSIC, the first electrodes were manufactured using Norit Activated Carbon with 8% polyvinylidene difluoride (PVDF) and 2% carbon black (CB) as binder.

Further research still needs to be done on porous carbon for screen printing on electrodes. INCAR-CSIC have developed a proprietary xerogel that can be used for this purpose. Another set of electrodes has been produced using this material instead of the commercial porous carbon.

The rest of the elements in the cells tested (exchange membranes and spacers) are commercial products: anionic exchange membrane (Fumasep FAS-30 10 x 10 from Fuel Cell Store), cationic exchange membrane (Fumasep FKS-30 10 x 10 from Fuel Cell Store), silicone/polypropylene spacer-gasket, 0.45-mm thick (ED 64-102-086 from PC Cell) and silicone/polypropylene end spacer-gasket, 0.45-mm thick (ED 64-102-085 from PC Cell).

## III. CELL MODEL

A CapMix cell like the one described in the previous section has an electrical behavior similar to that of a supercapacitor. The ion adsorption that takes place at the electrodes creates a double-layer structure that justifies such performance. Therefore, in order to electrically analyze the operation of these cells, it is possible to apply the already existing models of supercapacitors that are currently being used in power-electronic applications [10].

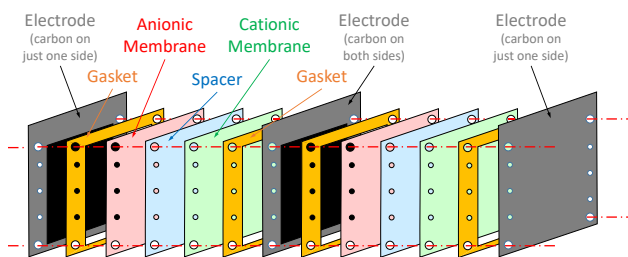


Fig. 4. Cell voltage and power in two subsequent cycles.

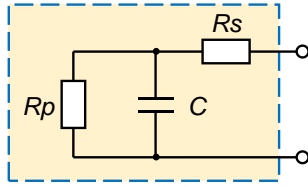


Fig. 5. Lumped-parameter model of a CapMix cell.

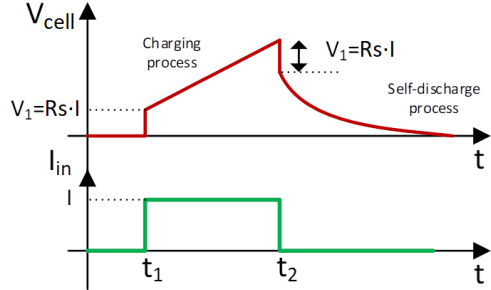


Fig. 6. Evolution of cell voltage during characterization of a CapMix cell.

In this work, a classical, lumped-parameter model will be used that consists of three components: a capacitor,  $C$ , where energy is stored, a series resistor,  $R_s$ , that represents ohmic losses when extracting the energy out of the capacitor, and a parallel resistor,  $R_p$ , that justifies the self-discharge of the cell (see Fig. 5). Simple as it is, this model allows designers to determine the performance expected from CapMix cells. More complicated models that include information on the physical phenomena taking place inside the cell might be developed, but that is beyond the scope of this paper.

To determine the value of the parameters in the lumped-component model of a given CapMix cell, saline water of a given concentration is pumped into an initially clean cell. This gives rise to a capacitor-like structure that must be characterized as indicated in Fig. 6. If a constant current,  $I$ , flows through the electrical terminals of the cell, the voltage will increase more or less linearly; this allows calculating the value of the equivalent capacitance,  $C$ . When the current is interrupted again, a self-discharge process can be observed that defines the value of the parallel resistor,  $R_p$ . The value of the series resistor,  $R_s$ , can be calculated from the voltage variation that occurs when the current starts/stops flowing (voltage  $V_1$  in Fig. 6).

The electrical equivalent of a two-electrode CapMix cell can thus be obtained. When several cells must be connected in series (to operate with higher voltages) or in parallel (to reduce overall series resistance and/or increase total capacitance), several lumped-parameter models must be conveniently connected. Fig. 7 shows one of these possible situations. Most of the times, the value of the parallel resistor,  $R_p$ , in the

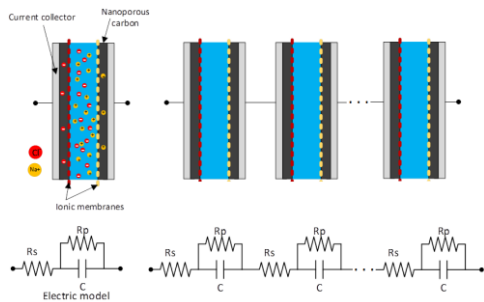


Fig. 7. Series association of several CapMix cells.

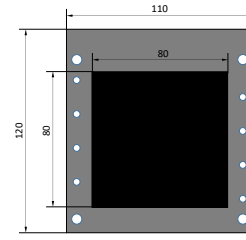


Fig. 8. Carbon screen-printed on the electrodes of the CapMix cell.

lumped model is high enough to neglect it, since it would have little influence in the overall performance of the cell.

It must be taken into account that each cell will be associated to two electrical models: one when salt water flows between its electrodes and another one for the case when fresh water is used. This is so because the water performs as dielectric (hence, a different  $C$  value will be defined) and because the conductivity of salt water is higher than that of fresh water (hence, different values for  $R_s$ ).

#### IV. CHARACTERIZATION OF THE CELLS

The CapMix cells used to conduct the research presented in this paper were manufactured with two isostatic graphite plates (11cm x 10cm x 2mm) on which porous carbon was screen-printed (8cm x 8cm x 300 $\mu$ m) as shown in Fig. 8. Two different sets of electrodes were used: those with commercial carbon and those with the xerogel manufactured by INCAR-CSIC.

Other than this difference in the carbon used, both CapMix cells were identical: same ionic exchange membranes and same spacers. The cells were characterized following the procedure described in the previous section. Fig. 9 shows the scope waveforms obtained while characterizing one of the cells. It can be checked that the result obtained matches that anticipated in Fig. 6.

Table II includes the values obtained for the parameters of each of the cells under test. As indicated above, the value of the parallel resistor,  $R_p$ , is not considered in the tests.

TABLE II. CELL PARAMETERS FOR DIFFERENT CARBON TYPES

	Commercial Carbon <sup>a</sup>		Xerogel by INCAR-CSIC <sup>a</sup>	
	Salt Water	Fresh Water	Salt Water	Fresh Water
$C$ [F]	24	14	25	12
$R_s$ [ $\Omega$ ]	0.220	5.3	0.187	2.5

<sup>a</sup>. Thickness of carbon screen-printed: 300 $\mu$ m



Fig. 9. Experimental characterization of a CapMix cell.

These results evince that the carbon used largely influences the performance of the CapMix cells. The xerogel developed by INCAR-CSIC has improved some features with respect to the commercial carbon. Additional research remains to be done to determine certain production features such as the right thickness to use or the optimum amount of binder included in the final material. Further improvements are still to come but, in this paper, only the two materials shown in Table II will be considered.

## V. ENERGY EXTRACTION

As explained above, the alternation of salt water and fresh water in a CapMix cell results in a certain amount of energy stored in the cell. This has already been presented several times in the literature [6-9]. What is not so easy to find is a work explaining how to efficiently extract that energy from the cell (most papers simply discharge that energy on a resistive load). Obviously, some kind of power-electronic converter will be needed to transfer that energy from the cell into some kind of storage element (namely a battery) of directly into the grid. Some research must be conducted in this topic. This paper aims to provide some insight into the requirements of such a converter based on the specific features of CapMix cells.

The authors consider that, since CapMix cells can be represented as a large capacitor, the best way to discharge the energy they may have in a controlled manner is by using a constant DC current. It might be sensible to think that large currents should be used, so that it only took a short time to discharge the cell and it were possible to charge it again so as to obtain the maximum possible amount of energy in a given time. Unfortunately, this is not so straight forward: the large series resistor in the CapMix cell would result in too high power losses if a large current were used. Some investigation must then be carried out to determine whether there is an optimum value for this discharge current.

Some simulations were run using PSIM with a simplified CapMix cell model being discharged at constant current (see Fig. 10).

Simulations started with the equivalent capacitor charged at  $V_{C0}=170\text{mV}$  for the case of a cell with commercial carbon and at  $V_{C0}=160\text{mV}$  for the case of a cell with the xerogel considered. These voltage values were empirically obtained by means of several tests performed in the lab with fresh water (the voltages obtained with salt water would be 130mV and 120mV respectively). This determines that the CapMix cell is initially charged with the energy in (1).

$$E_{C0} = 0.5 \cdot C \cdot V_{C0}^2 \quad (1)$$

The tests performed assume that a current  $I$  is used to discharge the energy of the cell, and that this process is stopped when the voltage across the cell is null ( $V_{\text{Cell}}=0$ ). This does not mean, however, that the cell has been fully

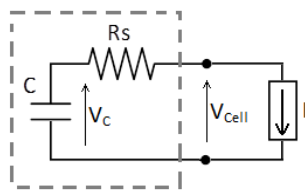


Fig. 10. Circuit considered to simulate the discharge of the CapMix cell.

discharged: if current  $I$  is interrupted at that moment, the cell voltage,  $V_{\text{Cell}}$ , will instantaneously take a value different from zero that corresponds to the voltage still present across the equivalent capacitor. This voltage, which will be referred to as “remaining voltage”,  $V_{C_r}$ , can be calculated as

$$V_{C_r} = R_S \cdot I \quad (2)$$

and allows defining the value of the energy that is not extracted from the cell when the procedure described above is followed:

$$E_{C_r} = 0.5 \cdot C \cdot V_{C_r}^2 \quad (3)$$

Therefore, thanks to the simulations, it is possible to calculate the value of the actual harnessed energy,  $E_{C_h}$ , for all the different cases. This energy will be calculated as the difference between the initial energy and the remaining energy minus the energy lost in the series resistor during the transfer:

$$E_{C_h} = E_{C0} - E_{C_r} - R_S \cdot I^2 \cdot t \quad (4)$$

$$E_{C_h} = 0.5 \cdot C \cdot (V_{C0}^2 - V_{C_r}^2) - R_S \cdot I^2 \cdot t \quad (5)$$

Fig. 11 shows the aspect of the plots obtained with the simulations run. It can be seen that current  $I$  linearly discharges the equivalent capacitor and that the voltage across the cell is a few volts lower (precisely,  $V_{C_r}$ ). The graph represents the case for fresh water but it would be the same for salt water, only with a different initial voltage.

The value of current  $I$  should be lower when dealing with fresh water, because the series resistance of the cell,  $R_s$ , is much higher in this case (refer to Table II) and current must be reduced to minimize power losses due to this resistance. Taking this into account, Table III includes the results obtained when running several simulations of one discharge considering both salt and fresh water flowing into CapMix cells manufactured with different types of carbon.

TABLE III. ENERGIES INVOLVED IN ONE DISCHARGE

		Salt Water ( $I = 100\text{mA}$ )	Fresh Water ( $I = 10\text{mA}$ )
Commercial Carbon	$E_o$ [mJ]	202.8	202.3
	$E_{C_r}$ [mJ]	5.8	19.7
	$E_{C_h}$ [mJ]	140.0	95.8
	$\eta$ [%]	69.0	47.4
Xerogel by INCAR-CSIC	$E_o$ [mJ]	180.0	153.6
	$E_{C_r}$ [mJ]	4.4	3.8
	$E_{C_h}$ [mJ]	128.3	109.4
	$\eta$ [%]	71.3	71.2

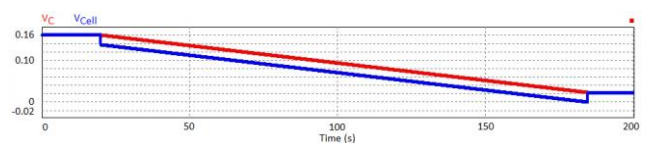


Fig. 11. Simulation results corresponding to one discharge of the cell.

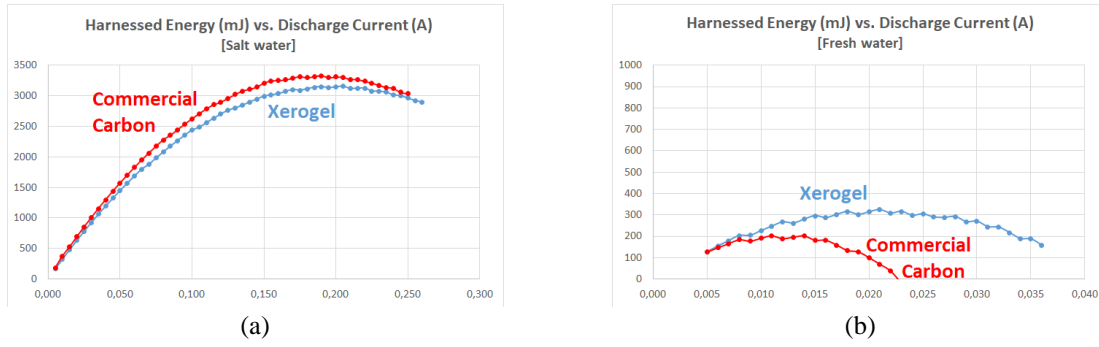


Fig. 12. Harnessed energy vs. discharge current. a) For salt water. b) For fresh water.

The results in Table III show the energies obtained when discharging a CapMix cell at a particular current. Further simulations with different values of current  $I$  should be run to determine whether an optimum value of this current can be obtained. However, in order to make a fair comparison, some considerations must be taken into account.

It has already been hinted that the discharge should be as fast as possible in order to be able to charge the cell again and produce as much saline gradient energy as possible. Time is thus an important parameter when determining the overall efficiency of the procedure. This is why the comparison of the results obtained with different discharge currents must be analyzed for a given unit time. Therefore, the harnessed energy,  $E_{C,h}$ , is first determined for the lowest current considered in the tests. This current also defines the longest time required to complete one discharge cycle. Taking this time as a reference, the tests with the rest of the currents are performed so that several charge-discharge cycles are carried out during a time as long as the “reference time” defined by the test run at low current. Thus, the comparison is not established on a one-cycle basis; instead, the harnessed energy per unit time will be determined with each current considered.

When following this procedure, it must be taken into account that having several cycles involves pumping water into the cell every time it must be charged again. This means that some time and energy is required for the charging, and this must be calculated.

The theoretical power consumed to pump water into the CapMix cell,  $P_{pump}$ , is calculated as

$$P_{pump} [W] = \Delta p [\text{kg/cm}^2] \cdot Q [\text{m}^3/\text{h}] \cdot 27.25 \quad (6)$$

where  $\Delta p$  is the pressure drop at the cell and  $Q$  is the pump flow rate. The values considered were those experimentally measured at a workbench that includes a pump operating at a flow rate of  $0.0144 \text{m}^3/\text{h}$  (100ml every 25s), which gives rise to a pressure drop of  $0.06 \text{kg/cm}^2$  in the CapMix cell under test. This results in a consumption  $P_{pump} \approx 23 \text{mW}$ .

However, it is not the pump power that must be calculated, but the energy, since this is the magnitude considered in the simulations. In order to do so, it must be taken into account that the carbon surface in the CapMix cell used is  $8 \text{cm} \times 8 \text{cm}$  (see Fig. 8). Since the two electrodes are placed  $0.5 \text{mm}$  away from each other, the volume of water needed to fill the space between both carbon surfaces is  $80 \text{mm} \times 80 \text{mm} \times 0.5 \text{mm}$ , which results in  $3,200 \text{mm}^3$ . With this volume, and knowing that the pump forces 100ml into the cell every 25s, it is simple to derive that it takes around  $0.8 \text{s}$  to fill the cell. Hence, the

energy required by the pump to charge the cell is calculated to be  $E_{pump} \approx 18 \text{mJ}$ .

Considering all this, it is possible to plot the amount of energy harnessed during this “reference time” as a function of the discharge current used. Fig. 12 shows the results obtained considering the CapMix cell is operating both with salt water and with fresh water. As already indicated, during continuous operation the discharge current must alternate between two values: one to be used when the CapMix cell has salt water inside and another one for the case when fresh water is used.

The two curves plotted in these graphs correspond to the two materials used for the electrodes: commercial carbon (red dots) and xerogel produced by INCAR-CSIC (blue dots).

Several things can be observed in these graphs:

- There is not so much difference in the performance of the xerogel and the commercial material when salt water is used. In fact, the commercial carbon seems to perform slightly better.
- There is a large difference, however, when considering the discharge with fresh water. It can be seen that the energy harnessed using the new material can get to be 60% larger than that obtained with the commercial product in this case.
- The energy obtained from the salt water cycle is far larger (almost by a factor of 10) than that corresponding to the fresh water cycle. Yet, it is not possible to dispense with the fresh-water discharge, since the alternation of salt and fresh water is essential for the correct performance of the cell.

In any case, it is obvious that the choice of the material used for the screen-printed carbon has an influence in the final performance of the cell. Further optimization of the xerogel manufactured by INCAR-CSIC is expected in a near future, which might contribute to even better results.

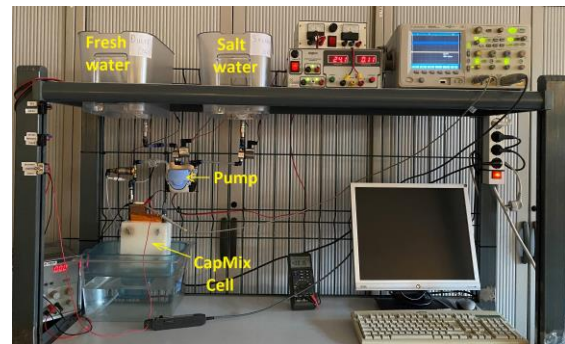


Fig. 13. Workbench used to test the CapMix cell.

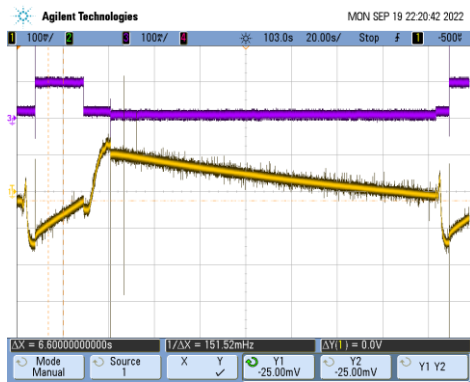


Fig. 14 Experimental discharge of the CapMix cell under test.

## VI. EXPERIMENTAL RESULTS

All the performance described in this paper has been tested on a workbench where water with different salt concentration is pumped into the CapMix cell under test (see Fig. 13).

Using this workbench, the simulation results obtained when discharging the energy stored in the cell could be checked. Fig. 14 shows such discharge for the case of a CapMix cell manufactured using xerogel. The waveforms obtained match the simulated results represented in Fig. 11.

This workbench will also be used to investigate the steady-state performance of CapMix cells, where cycles of charge-discharge must be continuously produced. Fig. 15 shows some preliminary results obtained so far.

## VII. CONCLUSIONS

The work presented in this paper deals with the practical operation of CapMix cells for energy harvesting by mixing sea and river water. Although this technology has been around for a few years now, most of the literature focuses on the physical phenomenon that enables this renewable source of energy, but with little or no emphasis on how to extract the energy captured.

Construction of the CapMix cell is one key issue in optimizing the energy extraction process. By using the adequate materials, cells that perform like large capacitors with low series resistance might be produced. The influence of the nanoporous carbon needed in the electrodes of these cells has been presented. Further research in this type of materials will result in better electrical features that will make the extraction of the energy stored more efficient.

As well as the characteristics of the cell itself, the procedure to efficiently extract that energy must also be

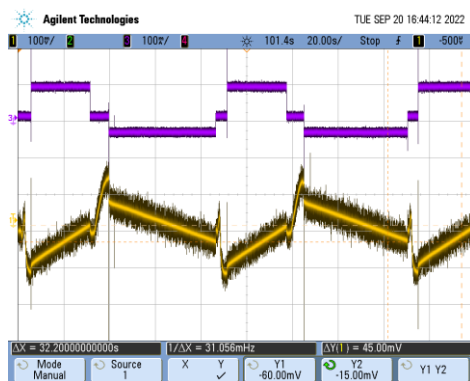


Fig. 15 Preliminary results for continuous energy harvesting.

considered. Since the voltages considered are in the order of the millivolts and the series resistance of the cell is typically large, the selection of the current used to transfer the energy from the CapMix cell into a battery (or into the grid, for that matter) becomes an important issue. An optimum value for this current has been obtained for the two discharge periods: the one corresponding to a cell being charged with salt water and that corresponding to fresh water.

Experimental results have been presented to validate the conclusions that were obtained through simulation.

Future works involve having a cell continuously producing energy by defining alternating cycles of salt and fresh water. Some preliminary results in this topic have already been obtained.

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