

Proof of concept of a zinc-silver battery for the extraction of energy from a concentration difference.

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Abstract

The conversion of heat into current can be obtained by a process with two stages. In the first one, the heat is used for distilling a solution and obtaining two flows with different concentrations. In the second stage, the two flows are sent to an electrochemical cell that produces current by consuming the concentration difference. In this paper, we propose such an electrochemical cell, working with water solutions of zinc chloride. The cell contains two electrodes, made respectively of zinc and silver covered by silver chloride. The operation of the cell is analogous to that of the capacitive mixing and of the “mixing entropy battery”: the electrodes are charged while dipped in the concentrated solution and discharged when dipped in the diluted solution. The cyclic operation allows us to extract a surplus of energy, at the expense of the free energy of the concentration difference. We evaluate the feasibility of such a cell for practical applications, and find that a power up to 2 W per m² of surface of the electrodes can be achieved.

1 Introduction

Salinity gradient power (SGP) is the production of renewable and clean power from naturally available water reservoirs with different salinity [30, 28, 24], e.g. river and sea water. SPG techniques can also be applied to solutions of salts, different from sodium chloride, whose concentration difference is produced by means of distillation [20, 10]. In the present paper, we focus on a zinc chloride solutions.

The two most mature SGP techniques are “pressure-retarded osmosis” [21, 23, 11], based on semi-permeable membranes, and “reverse electrodialysis” [42, 32, 31], based on ion-exchange membranes. In order to avoid such expensive membranes, a new family of electrochemical techniques have been recently introduced: nanoporous materials are used as capacitive electrodes in the “capacitive mixing” (CAPMIX) technique [5, 37, 7, 8, 4, 22, 9, 36, 34], while battery electrodes undergoing redox reactions are used in the “mixing entropy battery” [20, 16] and in the concentration cell proposed in [12]. Since capacitors and batteries are collectively called accumulators, this family of techniques will be called “accumulator mixing” (AccMix). The device described in the present paper (see Sect. 2) belongs to this family, being based on a zinc-silver chloride battery [18, 13]; it is designed for working with zinc chloride solutions.

The application of SGP techniques to artificially produced concentration differences has been limited, up to now, to the recovery of by-products of other processes [25, 3], or even wastes such as CO₂ [15]. Recently, it has also been proposed to use an SGP device in a closed cycle in which the concentration difference is obtained by means of distillation [20, 10], see Fig. 1. The whole process is actually a heat-to-current converter working in closed-cycle with respect to the solutions. The first stage of the process, aimed at the regeneration of the concentration difference, including the distiller, is not in the scope of the present paper and was already discussed in [10].

In that paper, we have shown that the use of solutions with high boiling point elevation leads to a high overall efficiency of the energy conversion. For exam-

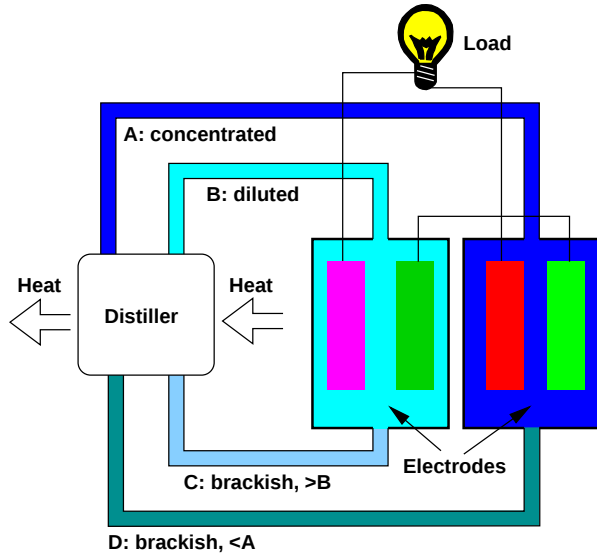


Figure 1: **Sketch of the heat-to-current converter system.** The electrochemical cells consume the concentration difference between two flows A and B, using the available free energy for producing an electrical current. The concentrations are then restored by means of a distiller, that consumes heat. The system is thus a heat-to-current converter.

ple, by making use of sodium hydroxide, the efficiency of the global process was theoretically estimated, on general thermodynamical grounds, to be of the order of 15%. The present paper focuses on another promising electrolyte, i.e. zinc chloride. Indeed, in such a case on the one hand the solute presents a high solubility and gives a high boiling point elevation (see Sect. 3), on the other hand the conversion of the salinity difference into electrical energy can be achieved by means of the efficient zinc-silver AccMix cell that is described in the present paper.

Another relevant feature of a heat-to-current current working with zinc chloride solution can easily work with low-temperature heat sources, i.e. in the range 80-130°C, as will be shown in Sect. 2. So this technique can become a promising one, with a wide range of applications, including solar energy production with thermal collectors [19, 27, 39], recovery of waste heat from industrial processes, cogeneration of electrical current and heat for domestic uses [35, 29]. Such techniques are particularly appealing for small-scale applications and can become competitive with the state-of-the-art solutions, such as Stirling motors, organic Rankine cycle turbines or thermoelectric elements, based on the Seebeck effect [38, 41, 14]. It's worth noting that a two stage heat-to-current converter, involving distillation of an ammonia/CO₂ solution and a pressure-retarded osmosis device has been proposed [26].

A proof-of-concept of our zinc-silver AccMix cell is described in Sect. 2. The boiling point, and its relation with the overall efficiency and the specific free energy of the solution, is discussed in Sect. 3. The equilibrium cell voltage is discussed in Sect. 4. The discussion of the kinetics and the measurement of the power production is presented in Sect. 5. In Sect. 6 we report some unwanted effects, leading to a reduction of the power production, which have been observed in some cases, but which can be avoided by operating the cell in a suitable regime.

2 AccMix cell for zinc chloride

In this section, we describe the implementation of an unusual SGP cell working with a zinc chloride solu-

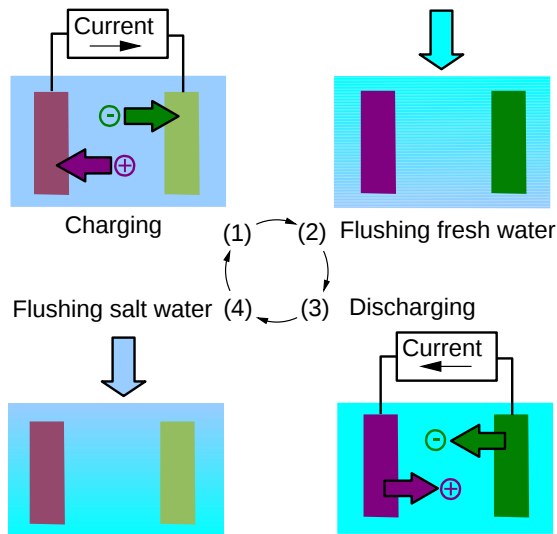


Figure 2: **Cycles of the AccMix technique.** The cycle starts with the cell filled with the high concentration solution. The phases are: (1) charge, (2) flow of dilute solution, (3) discharge, (4) flow of concentrated solution.

tion, a good candidate for the closed-cycle heat-to-current converter based on SGP technology. The cell is operated with AccMix cycles, and is inspired by the zinc-silver chloride battery, that is known as one of the primary batteries with the highest power density [18, 13].

Figure 1 shows a couple of AccMix cells, one for each of the two flows at different concentrations. The voltages of the two cells are different, due to the different chemical potentials of the ions in the two solutions. For this reason, a current will flow through the load. This current cannot flow indefinitely, because the electrodes in the cell at lower concentration will be continuously consumed, and simultaneously the ions will deposit on the electrodes in the higher concentration cell. For this reason, the flows must be cyclically exchanged.

Focusing on one of the cells, the cycle is shown in Fig. 2. Each cell will thus undergo an AccMix cycle, analogous to the cycles seen in CAPMIX and in the “entropy mixing batteries”.

The energy comes from the voltage rise that takes place when the solution concentration is changed, that is given by Nernst equation: the charge is put into the cell at a lower voltage than that at which it is then extracted. We have shown that the voltage is connected with the adsorption of the solute during the step of the cycle in concentrated solution, and its release in the diluted solution [33]: the mixing is actually mediated by the temporary adsorption of the ions inside the electrodes. The energy is extracted at the expense of the concentration difference.

The AccMix cell is basically an accumulator, i.e. a battery or a supercapacitor, because it must accumulate the charge during the step A and give it back during the phase C. However, not all the battery electrodes feature a voltage rise, i.e. a change of voltage upon concentration changes, or, equivalently [33], an adsorption of ions during the charge or discharge step. For example, in a usual lithium ion battery, the lithium ions are released by one electrode and adsorbed by the other, both in charge and discharge steps, and thus the current flow does not induce a net release or adsorption of ions in the electrodes. For this reason, in the case of the AccMix cell that has been proposed for lithium chloride solutions, the manganese oxide (a typical positive electrode for lithium-ion batteries) has been coupled to a silver / silver chloride electrode, that interacts with chlorine ions [20]. During the charge, sodium and chlorine ions are adsorbed into the electrodes, and they are later released during the discharge.

It’s worth noting that the cell voltage, i.e. the potential difference between the electrodes, has no relevance in AccMix cycles. Indeed, there would be a technological advantage in having a cell voltage close to zero, or even that the cell voltage changes polarity upon the concentration change [6].

In order to find good electrodes for the zinc chloride solution, we can profit from the wide literature about rechargeable batteries. However, the requisites of our electrochemical cell are different from the requisites of a usual rechargeable battery. The energy that is extracted in each cycle is of the order of $Q \Delta V$, where Q is the charge that is exchanged in each cycle, and the voltage rise ΔV is quite small (of the order of a fraction of one V). For this reason, the losses must

be extremely small. Some of the requirements are:

1. The electrical charge efficiency of the charge/discharge cycles must be excellent: low self-discharge, i.e. low electrical charge leakage (it's an issue mainly for the supercapacitors electrodes based on activated carbon in the CDLE technique).
2. The energy efficiency of the charge/discharge cycles must be extremely high: low overvoltage.
3. Extremely high number of cycles.

For reaching these parameters, we must use charge and discharge currents that are much less than the currents usually applied in rechargeable batteries, and apply them for much shorter times. It is thus necessary to study the behaviour of the cells under very unusual conditions, and such information is often lacking in literature.

In the AccMix cell presented in this paper, one of the electrodes is a zinc foil, and the other is a silver foil or felt, covered with silver chloride. The electrolyte is a water solution of zinc chloride, concentrated and diluted as necessary in steps A and C.

The interest in such an electrochemical cell stems from the fact that a cell with similar electrodes is used as a primary battery, with an excellent power density. A second reason of interest is that zinc chloride has an extremely high solubility in water, and leads to a very high boiling point elevation. This property is connected with a high efficiency of the whole energy conversion cycle [10].

The electrodes are 0.1 mm-thick 1×1 cm foils (Alfa Aesar). The silver electrode is covered by silver chloride by means of anodization, that is performed at 3 mA in a 3 M sodium chloride solution for 1 hour. As an alternative, a silver wool, made of 100 μm wires, is employed; before the anodization, it is shaped as a 1×1 cm felt, around 1 mm thick.

The electrodes are kept at a distance of 0.6 mm, spaced by means of two nylon wires, and clamped between two current collectors made of graphite slabs 1 mm thick.

The solutions are obtained by dissolving zinc chloride (Alfa Aesar) in deionized water. The pH of the solution is adjusted by adding 1% in mass of HCl.

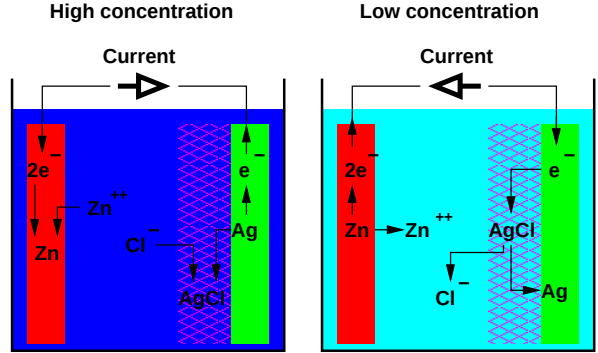


Figure 3: **AccMix cell for zinc chloride.** The reactions taking place in the two steps of the AccMix cycle are shown. Legend: ■ Concentrated zinc chloride solution; ■ Dilute zinc chloride solution; ■ Zinc electrode; ■ Porous silver chloride; ■ Silver.

The reactions taking place in the cell during the AccMix cycle are shown in Fig. 3. The charging step (passive phase) takes place when the cell is filled with the more concentrated solution. The current flows from the zinc electrode to the silver electrode. On the zinc electrode, zinc ions from the solution are reduced to metallic zinc. The silver electrode is oxidized, releasing silver ions that immediately precipitate forming a silver chloride porous film on the surface of the electrode. The discharging step (active phase) takes place when the cell is filled with the less concentrated solution. The current flows from the silver electrode to the zinc electrode. The zinc electrode is oxidized, and the zinc ions are released into the solution. The silver chloride on the surface of the silver electrode is reduced, giving metallic silver and releasing chloride ions into the solution.

It is evident that zinc chloride is temporarily stored into the electrodes during the step in higher concentration, and is later released into the less concentrated solution: we are actually performing an accumulator-mediated mixing, i.e. an AccMix cycle. This implies [33] that the cell, along the cycle, produces energy.

The traditional scheme of the AccMix cell [5, 20]

refers to a single cell, that is filled in different phases with the two solutions at different concentration. In a real working prototype, it will be useful to use a couple of cells, performing cycles at 180° , as shown in Fig. 1. In this way, one of the cells produces energy, part of which is consumed by the other. However, since the electrodes undergo accumulation or dissolution, the solution flows must be periodically exchanged, in order to invert the accumulation and dissolution: it is thus clear that the energy production is actually obtained, also in this case, by an AccMix cycle. In other words, the couple of cells is analogous to a mechanical engine with two cylinders and pistons: the active phase of one section of the engine drives the passive phases of the other section, but the energy production can be however evaluated by studying a single cylinder and piston. Indeed, this is what we show in Fig. 3: in the present paper, we make experiments on a single cell.

3 Boiling point elevation

The choice of the solution, i.e. zinc chloride in water, is based on the evaluation of the overall efficiency of the conversion of heat into current. Indeed, as already recalled, in [10] it was shown that, in order to increase the efficiency, a solute with a high boiling point elevation should be preferred [10]. The elevation of the boiling temperature of solutions of zinc chloride in water is reported in Fig. 4 (data provided by Italshell [1]). In this graph, and throughout this paper, the concentration is reported as the ratio between the mass of zinc chloride with respect to the total mass of the solution. The boiling point elevation that can be obtained is quite high, and thus this solution is promising. For ideal solutions, the boiling point elevation is expected to be $K_b b_{solute} i$, where K_b is the ebullioscopic constant (0.512 K Kg/mol) for water, b_{solute} is the molality of the solute, and i is the van 't Hoff factor. This formula predicts a linear dependence of the boiling point elevation at low concentrations. Instead, the actual boiling point elevation increases much more than linearly. This effect can be explained by assuming activity coefficients significantly different from 1, and considering that the

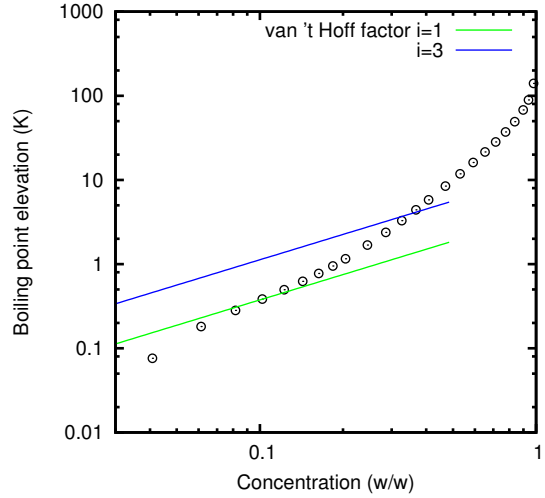


Figure 4: **Boiling point elevation of the ZnCl_2 solutions at 1 atm pressure.** Data provided by Italshell [1]. The concentration is expressed as the ratio between the mass of the solute and the total mass of the solution. The lines are the linear approximation for dilute solutions, for two different values of the van 't Hoff factor. The actual boiling point elevation has an evident deviation from the ideal solution, also at low concentrations. A quite high boiling temperature is observed in concentrated solutions.

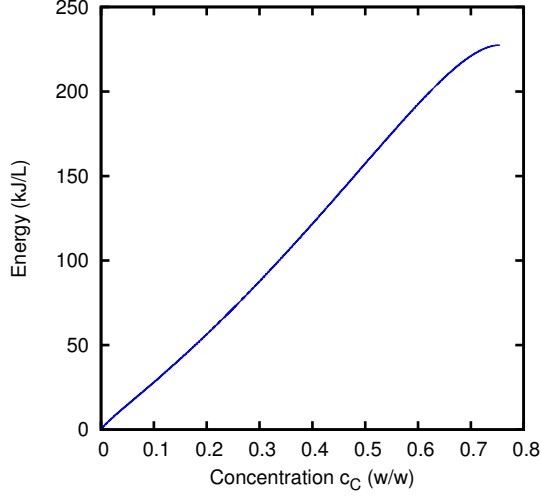


Figure 5: **Available free energy.** The graph shows the energy that can be ideally produced by a cell per liter of solvent in the diluted solution, as a function of the concentration of the outgoing diluted solution. The concentrated solution has a mass fraction $C_A = 75.5\%$, considered constant during the cycle, $c_D = c_A$. The step of the cycle in dilute solution starts with the cell filled with fresh water, $c_B = 0$, and stops at a concentration c_C .

zinc chloride forms complexes.

Working with solutions at about 0% and 80%, we expect a theoretical efficiency of 10% with a single-effect distiller [10]. Working at atmospheric pressure, the solution evaporates at 140°C and condenses at 100°C . However, the pressure can be reduced, as usual in distillation plants, so that the two temperatures become respectively around 80 and 45°C . An actual thermic device, reaching the above-mentioned efficiency, has been designed by Italschell [1].

The boiling temperature as a function of the concentration allows us to evaluate the free energy of the solution [10]. The free energy that is lost by the solutions, during the AccMix cycle, is converted into electrical current. An ideal way to operate the cell, for which the efficiency of this conversion could reach

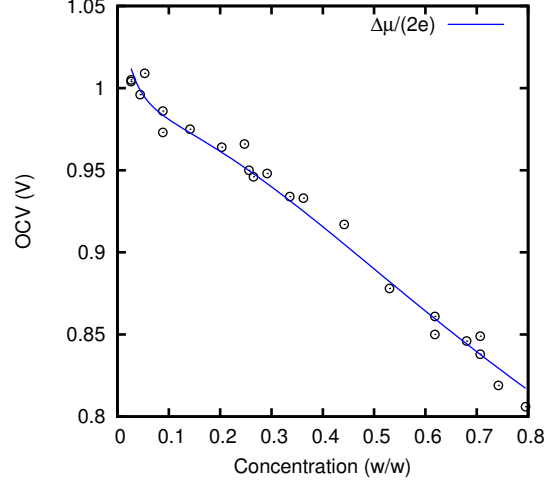


Figure 6: **Cell voltage as a function of the concentration.** The voltage is measured in open circuit. The solid line has been obtained from the chemical potential, in turn calculated from the boiling point elevation.

the maximum theoretical value, is the following. The flow rate of the concentrated solution, at concentration c_A , is so high that its concentration does not change significantly during its passage through the cell, so that $c_D \approx c_A$. The other flow from the distiller is pure water, $c_B = 0$, and the solution exits from the cell at concentration c_C . The reduction of free energy, corresponding to the electrical energy that could be extracted by means of such an ideal cycle per liter of solvent in the diluted solution, is shown in Fig. 5 as a function of c_C , for $c_A = c_D = 75.5\%$.

4 Cell voltage and voltage rise

We measured the cell voltage in open circuit. The result is shown in Fig. 6.

The solid line is calculated from the boiling point elevation curve. This curve actually allows us to evaluate the derivative of the Gibbs free energy with respect to the number of units of ZnCl_2 that are dis-

solved in the solution [10]. This quantity represents an “overall” chemical potential μ of the solute.¹ The passage of a pair of electrons through the cell leads to the adsorption or release of a unit of ZnCl_2 . Assuming that the cell works reversibly, we expect to observe a cell voltage $E = \Delta\mu/(2e)$, where $\Delta\mu$ is the difference between the chemical potential in the solution and that (assumed to be constant) on the electrodes in the solid state. This fact can be rigorously shown in terms of Nernst equation; indeed, the “overall” chemical potential μ corresponds at equilibrium also to the chemical potential of the undissociated molecule ZnCl_2 and to the sum of the chemical potentials $\mu_{\text{Zn}^{++}} + 2\mu_{\text{Cl}^-}$ of the dissociated ions Zn^{++} and Cl^- , also if the dissociation is not complete, or complexes such as ZnCl_3^- [17] are formed.

It must be noticed that the boiling point elevation allows us to evaluate only the variation of the chemical potential μ with respect to the concentration; the values are thus adjusted with a suitable additive constant.

In Fig. 6, it can be noticed that the open circuit cell voltage is indeed very close to $\Delta\mu/(2e)$. This shows that, at least in quasi-stationary conditions with a low current, the AccMix cell can work close to reversibility, i.e. it can in principle extract an energy equal to the overall reduction of the free energy of the solutions. The voltage rise, that is one of the main parameters of the AccMix cell, is the difference between the cell voltages at the concentrations of the feed solutions.

It can be noticed that the cell voltage is nearly linear in the concentration, and quite different from the logarithmic dependence that would be expected by approximating the activities with the concentrations. However, this is not surprising: at the highest concentrations that we consider the solution is mainly composed by zinc chloride, and water is the minor component.

¹This quantity is defined as “overall” because it does not refer to an actual chemical species present in the solution. Indeed, the solute is actually present in various forms: ions Zn^{++} and Cl^- , undissociated molecule ZnCl_2 , and various complexes, e.g. ZnCl_3^- .

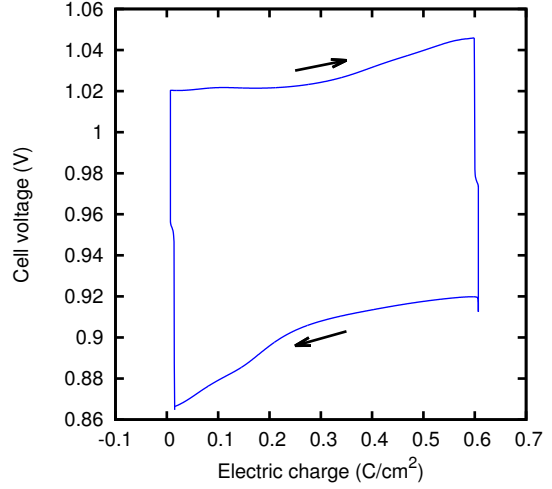


Figure 7: **Example of charge-discharge cycle.** The cycle is clockwise.

5 Electrokinetics measurements and AccMix cycles

We characterized the kinetic behaviour of the cell by means of charge/discharge cycles performed at constant concentration, at various values of the current. The cycles were composed by a charge phase at a given positive constant current for 60 s, followed by a discharge phase at the opposite current for 60 s. The cycle duration was chosen in order to mirror the actual duration of the typical AccMix cycles. The dissipated power is evaluated as the average of the product of the current and voltage over five cycles. The cycles can be effectively represented by plotting the cell voltage as function of the electric charge which has flown through the cell (i.e. the integral of the current with respect to time). An example of such a plot is given in Fig. 7. The energy dissipated during a cycle is equal to the area enclosed by the path.

The measured power dissipation is shown in Fig. 8. It can be noticed that the power dissipation is slightly higher at 68% concentration. This can be explained by considering that the resistivity of the ZnCl_2 solu-

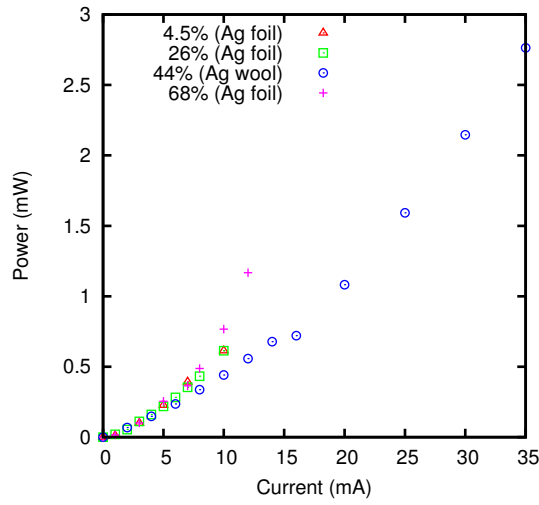


Figure 8: **Average dissipated power during charge-discharge cycles in ZnCl_2 solutions.** The various data sets refer to different concentrations and different electrodes. The size of the electrodes is 1×1 cm; in the case of the the Ag wool, this is the macroscopic dimension of the felt.

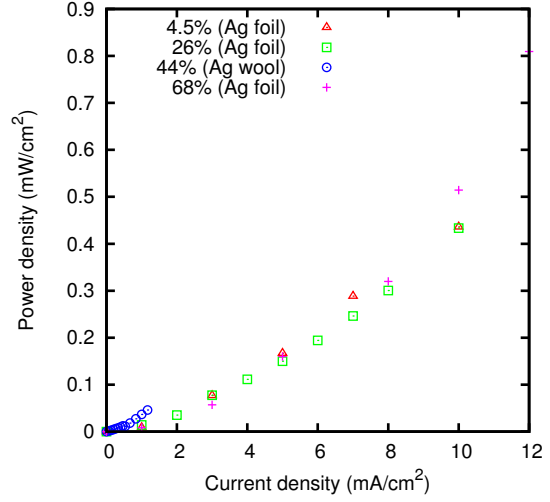


Figure 9: **Average dissipated power density at AgCl/Ag electrode.**

tion has a minimum of $0.1 \Omega\text{m}$ at 3.7 M concentration [40], and it increases at higher concentrations, e.g. it is $1.3 \Omega\text{m}$ at 80% .

The power dissipation is lower in the case of the felt obtained with the silver wool, in agreement with the larger effective surface: that is approximately 15 cm^2 for the $1 \times 1 \text{ cm}$ felts we used.

By means of a reference electrode, we tried to roughly measure the potentials of the single electrodes of the cell, in order to evaluate their individual contributions to power dissipation (the contribution of the resistance of the solution, although still visible in the case of the 68% solution, is relatively small).

The power dissipation at the Ag/AgCl electrode is reported in Fig. 9, expressed in terms of current per unit surface. It can be noticed that the power dissipation in the case of the silver wool is higher; this means that the geometric surface of the wires is not completely available for the reaction. It is possible that the silver chloride film, that forms during the anodization, insulates a part of the microwires forming the silver wool with respect to the others, and with respect to the current collector.

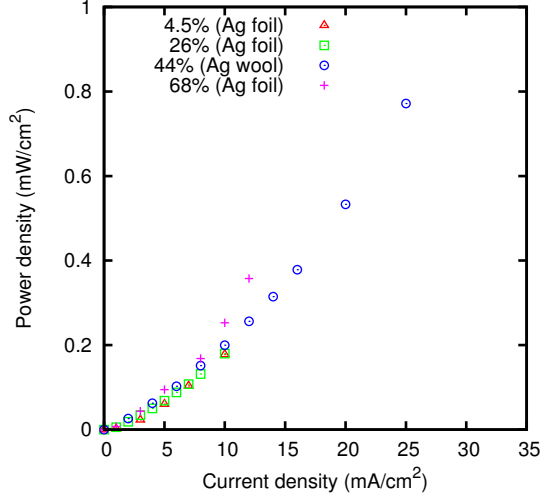


Figure 10: **Average dissipated power density at Zn electrode.**

The power dissipation at the zinc electrode is reported in Fig. 10. It can be noticed that the dissipation on the zinc electrode is less than the dissipation on the silver electrode, which thus represents the current bottleneck of the technique.

With our experimental setup we performed a series of AccMix cycles, which were composed of a charge phase of 60 s in concentrated solution at a given current, and a discharge phase of 60 s in diluted solution at the opposite current. Between any two consecutive phases of this type (the “active” phases of the cycle) there was an interval of 60 s at 0 current, during which we could transfer the electrodes from the container of the concentrated solution to that of the diluted solution or vice-versa. A plot of such a series of cycles in the (Q, V) plane is shown in Fig. 11. At variance with the charge-discharge cycles of Fig. 7, here the cycles are counterclockwise, and the enclosed area represents an energy which is delivered by the cell to the external circuit. The average produced power was calculated as the ratio between the average produced energy per cycle and the sum of the durations of the two active phases of the cycle (120

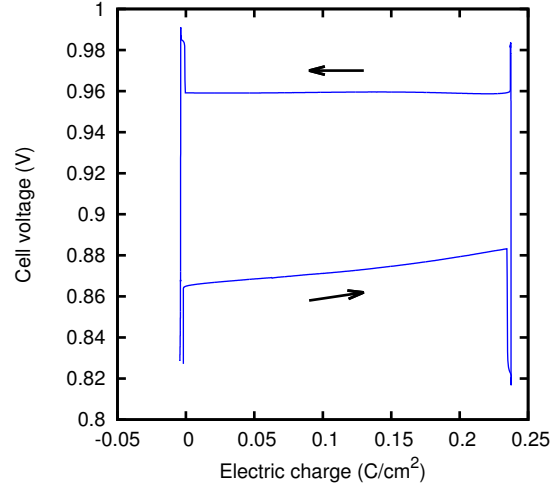


Figure 11: **Example of AccMix cycle.** The cycle is counterclockwise. The voltage rise is approximately 160 mV. The overvoltage, that reduces the cycle’s surface, results from the flowing current of 4 mA.

s in our case), therefore neglecting the intervals required for the transfer of the electrodes.

We measured the power production at various current intensities. The results are shown in Fig. 12. A maximum of approximately 2 W per square meter of electrode is obtained.

6 Silver chloride film

The behavior of the electrodes apparently keeps memory of their recent history. This was seen in some particular cases of charge–discharge cycles as those described in Sect. 5. In Figs. 13-14 we show two series of such cycles which were performed under slightly different conditions. In the first case, we see that the potential increases near the end of the charging phase, and that such an increase occurs closer and closer to the end of the phase, as cycles are repeated. In the second case we see instead that a potential fall occurs closer and closer to the end of the discharge phase. A possible interpretation of

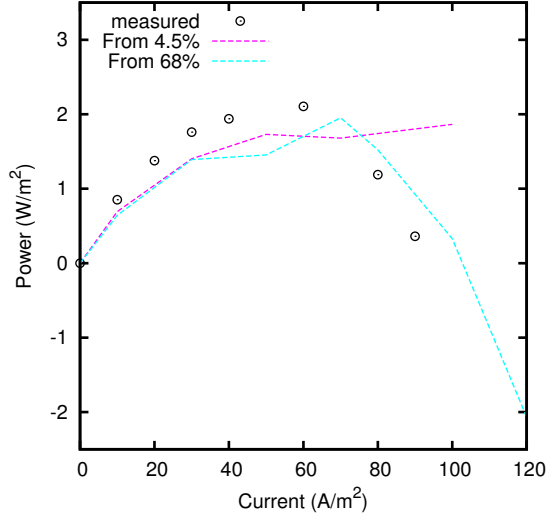


Figure 12: **Average gained power in AccMix cycles.** The concentrations of the ZnCl_2 solutions are $c_A = 4.5\%$ and $c_C = 68\%$. The lines represent an evaluation of the power production obtained by subtracting the power dissipation, measured during charge/discharge cycles, from an “ideal” power production, obtained by assuming a voltage rise of 160 mV and no overvoltage.

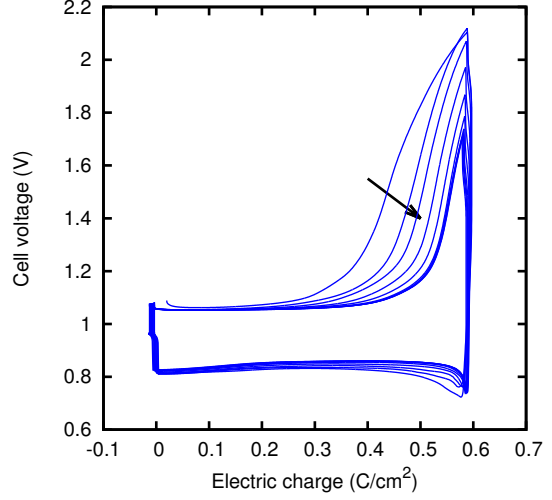


Figure 13: **Charge-discharge cycles with voltage increase at the end of the charge phase.** The cycles are clockwise. The arrow shows the reduction of the peak with time.

such a behavior is that during the charging phase silver chloride grows more easily at sites from which it has just been removed in the preceding cycles, and similarly that during the discharge phase silver chloride is more easily removed from sites in which it has just been grown in the preceding cycles. It is however difficult to systematically reproduce these phenomena. The best performance is of course obtained when either the potential increase in the charge or the potential fall in the discharge are avoided, and the cycle is represented by a roughly regular parallelogram in the (Q, V) plane. In this case in fact the area of the plane enclosed by the cycle, which represents a dissipated power, is minimized.

7 Conclusions

We have shown that our AccMix cell is efficient in converting the free energy of the zinc chloride solution into electrical current. The fact that the open-circuit voltage practically coincides with the value

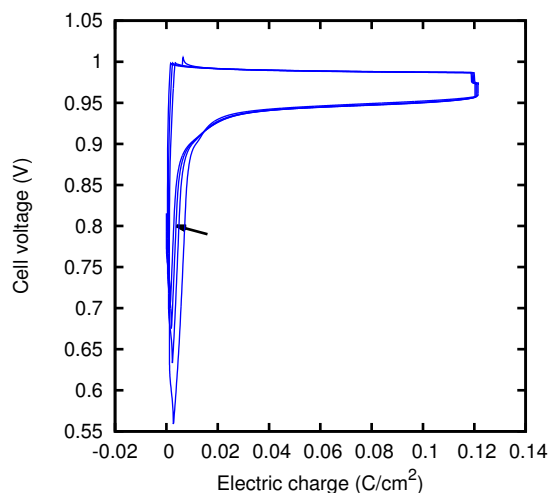


Figure 14: **Charge-discharge cycles with voltage fall at the end of the discharge phase.** The cycles are clockwise. A strong deviation from the rectangular shape of the cycle is evident at the end of the discharge phase (the branch at lower voltage).

theoretically expected from thermodynamical considerations (Fig. 6) means that the efficiency actually approaches unity as the current goes to zero. The maximum power production we achieved is around 2 W per square meter of electrode. By using microporous materials, e.g. sintered powders, we can have a surface of the order of $100 \text{ cm}^2/\text{g}$; this leads to a cost of the order of ten euros per W. This is a relatively good result: for comparison, reverse electrodialysis applied to sea and river water gives a power output of the order of 1 W per square meter of couple of membranes, having a cost of the order of 100 euro each.

As already noticed, the bottleneck of the system is the silver/silver chloride electrode. For this reason, further improvements might be obtained by replacing the silver electrode with other materials interacting with chlorine ions, e.g. conducting polymers like polypyrrole.

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