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Boosting the voltage of a salinity-gradient-power electrochemical cell by means of complex-forming solutions

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We report experiments on a concentration cell with zinc electrodes and ZnCl_2 solutions at different concentrations, separated by a porous diaphragm. The cell is aimed at the conversion of the free energy associated to the concentration difference into electrical energy, for renewable and clean energy applications. Usually, the diffusion of the solute across the diaphragm constitutes a waste of free energy, which impairs the voltage generation of the concentration cell with respect to other well-known techniques that work quasi-reversibly, such as reverse electrodialysis or the “mixing entropy battery.” Quite surprisingly, we find that the voltage produced by our concentration cell is significantly *higher* than the voltage obtained with the other quasi-reversible techniques. We show that the surplus voltage comes from the active transformation of the mixing free energy into electrical energy performed by the liquid junction, and we show the connection with the negative apparent transference number of the zinc ion. This fortunate consequence of using ZnCl_2 solution is ultimately related to the formation of complexes. We present the results of a cell for power production, which has excellent performances with respect to known salinity-difference-power methods.

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The salinity gradient power (SGP), i.e., the conversion of the free energy associated to a concentration difference into electrical power or mechanical work, has attracted the interest of the scientific community, because of its potential use for producing clean and renewable energy. Besides the naturally occurring salinity difference sources, like seas and rivers,^{1–4} it has been proposed that the concentration difference can be produced artificially by means of distillation.^{5–7} In this case, the SGP is used as an intermediate step of the production of electrical current from low-temperature heat sources (possibly, solar or waste heat).

In this Letter, we focus on a solution of zinc chloride in water. The primary reason for this choice is that, in order to achieve a high overall efficiency of the heat-to-current conversion, one needs to use a solution with a high boiling point elevation ΔT .⁷ Due to the great solubility of zinc chloride, ΔT can be as high as 40 °C, i.e., one can have an efficiency of the order of 10%. However, we will show that this solution also leads to other advantages, when used in the cell here described.

The most studied electrochemical SGP technique is the “reverse electrodialysis” (RED),^{8–10} based on the Donnan potential across ion-exchange membranes. Alternatives have been recently proposed, in order to avoid the expensive membranes: the “accumulator mixing” (AccMix) techniques, based on the voltage rise that occurs when one changes the concentration of the solution in which a couple of battery-like (“mixing entropy battery”^{5,11,12}) or supercapacitor-like (“capacitive mixing,” CAPMIX^{4,13–17}) electrodes are dipped.

Ideally, all the above-mentioned techniques can work quasi-reversibly, i.e., with a negligible free-energy loss, and thus their open-circuit voltage can be considered as the “reversible voltage” ΔV_{rev} of the SGP cell. In this situation, the produced electrical energy equals the decrease of free

energy associated to the concentration difference of the solutions. On one hand, the migration of 1 mol of salt from the more to the less concentrated solution leads to a decrease of the free energy equal to the variation of the chemical potential $\Delta\mu = \mu_H - \mu_L$, where μ_H and μ_L are the chemical potentials of the salt in the more and less concentrated solutions. On the other hand, the free energy is converted into the electrical energy $zN_A e \Delta V_{rev}$, where z is the number of moles of charges involved in the migration of 1 mol of salt, N_A is the Avogadro’s number, and e is the absolute value of the electron charge. We thus obtain $\Delta V_{rev} = \Delta\mu / (zN_A e)$, in accordance with Nernst law, expressing the (quasi-)reversibility of the process.

The cell described in the present Letter is a concentration cell (CC), i.e., it is composed by two semi-cells, separated by a porous diaphragm, filled with solutions at different concentrations in which identical electrodes are dipped. The diffusion across the diaphragm gives a continuous loss of free energy. This generally leads to an open-circuit voltage less than ΔV_{rev} that is the reason why the CC is generally not popular as SGP device. For example, in experiments with NaCl solutions, the effective open-circuit voltage of RED and AccMix devices is close to the reversible voltage ΔV_{rev} , while the voltage of the CC¹⁸ is about one half the ΔV_{rev} : it is often explained by saying that the CC only uses one of the ions.

In the case of ZnCl_2 , we recently reported an AccMix cell¹² giving a voltage very close to the reversible voltage ΔV_{rev} . Quite surprisingly, the CC for ZnCl_2 reported here gives a voltage significantly exceeding ΔV_{rev} , rather than much lower as usually happens. We provide evidence that the surplus voltage is due to the active transformation of the free energy of mixing into electrical energy, taking place in the liquid junction, due to the formation of complexes. We

quantitatively express this concept in terms of transport properties of the solution, already reported as a negative apparent transference number of zinc.¹⁹

Finally, we describe a CC for power production. We show that it has excellent performances in terms of power production per square meter of electrode, and it has by far the lowest cost per unit power among the known SGP techniques.

Figure 1 shows a sketch of the CC with zinc electrodes (panel (a)) and with Ag/AgCl electrodes (panel (b)). The cells contain the feed solutions of ZnCl_2 in water, at concentrations c_L and c_H . The voltages are called ΔV_{Zn} and $\Delta V_{\text{Ag/AgCl}}$, respectively. The solutions are put into contact through a porous diaphragm constituted by filter paper. At variance with reverse electrodialysis, the diaphragm is not perm-selective, but allows the diffusion and transport of any ion; its role is simply to avoid the advective mixing of the solutions.

In the CC with zinc electrodes, the reaction $\text{Zn}^{++} + 2e^- \rightleftharpoons \text{Zn}$ reaches an equilibrium; for the Ag/AgCl cell, the reaction is $\text{Ag} + \text{Cl}^- \rightleftharpoons \text{AgCl} + e^-$. Due to the different activities of the ions in the two semi-cells, a difference of potential is present between the electrodes: it can be used for generating a current in the load, i.e., for producing power. On the electrodes, the flow of such current induces the adsorption of ions in the more concentrated solution and the release of ions in the less concentrated one. The flow of the current is closed through the porous diaphragm, where it actually consists in the transport of ions, including Zn^{++} and Cl^- ; ZnCl_2 forms various charged complexes which also take part to the current flow. We thus have an overall migration of the salt from the more to the less concentrated solution: the electrical power is actually provided to the load at the expenses of the free energy associated to the concentration difference of the solutions. In a cell aimed at the power production, the ions accumulate on one electrode while the other electrode is consumed. Thus, the electrodes must be periodically exchanged in order to avoid the complete consumption of one of them.

In Fig. 2, we report the voltages ΔV_{Zn} and $\Delta V_{\text{Ag/AgCl}}$ of the CCs with zinc and Ag/AgCl electrodes, respectively.

The graph also reports the reversible voltage $\Delta V_{\text{rev}} = \Delta\mu/(2N_Ae)$. It represents the open-circuit voltage of an ideal reversible SGP device, working with ZnCl_2 , in

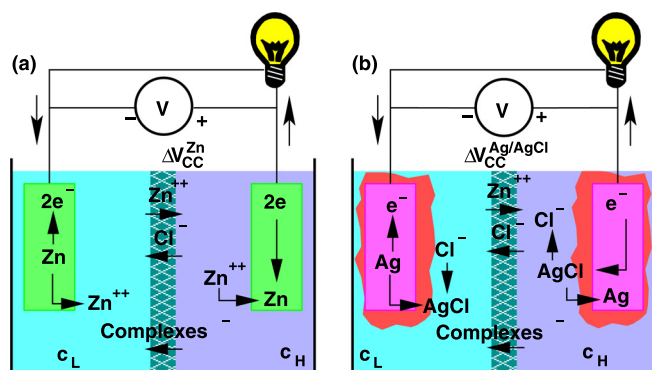


FIG. 1. Experimental setup. Panel (a): concentration cell with Zn electrodes. Panel (b): concentration cell with Ag/AgCl electrodes.

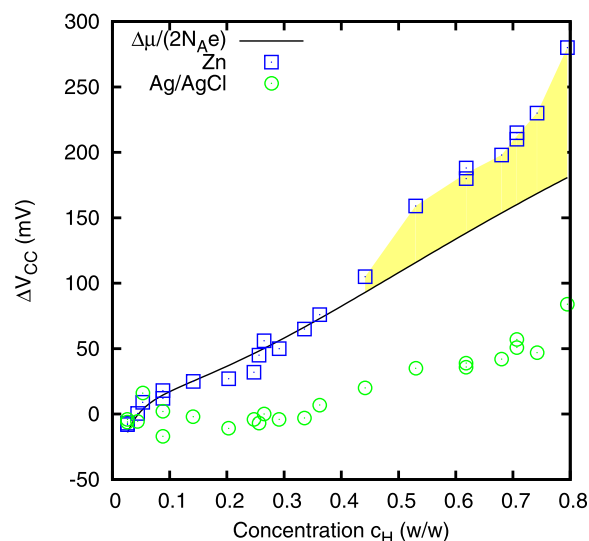


FIG. 2. Voltage of the concentration cell, measured as a function of the concentration c_H of the high-concentration compartment. Squares and circle refer to the cell with zinc and silver electrodes, respectively. The concentration in the low-concentration compartment is fixed, $c_L = 5\%$. The solid line reports the reversible voltage $\Delta\mu/(2N_Ae)$.

which exactly 1 mol of salt migrates per each couple of moles of electrons that flow. The solid line represents $\Delta\mu/(2N_Ae)$, calculated from osmometric measurements of the chemical potential.⁷ We already reported that the measurement of the open-circuit potential of an AccMix cell is actually very close to this curve,¹² thus showing that the AccMix cell is nearly reversible. We do not report RED measurements because the behavior of the ion-exchange membranes with the complex-forming ZnCl_2 solution is questionable.

In Fig. 2, it can be noticed that the zinc CC voltage ΔV_{Zn} is significantly larger than ΔV_{rev} , more than 1.5 times at 80% concentration. This result is surprising because the voltage of the CC is usually much lower than the voltage of the reversible electrochemical SGPs. Moreover, the result means that the electrical energy carried by two moles of electrons that flow through the cell is more than the variation of the chemical potential of 1 mol of salt due to the migration from the more to the less concentrated solution. From the second principle of thermodynamics, this implies that more than 1 mol of salt migrates when 2 mol of electrons flow. This is not surprising, because the migration can easily take place across the porous diaphragm; however, this raises the question of how and where the migration of the ions is converted into electrical energy.

A first clue for explaining the puzzling phenomenon can be found in the other quite surprising observation that the voltage $\Delta V_{\text{Ag/AgCl}}$ of the Ag/AgCl CC is positive (see Fig. 2), i.e., the potential of the Ag/AgCl electrode is higher in the more concentrated solution. Instead, the Nernst equation would predict a positive value for the zinc electrode and a negative value for the Ag/AgCl electrode. This result suggests that a huge liquid junction potential, of the order of 100 mV, develops across the diaphragm, and is strong enough to reverse the polarity of the cell. We argue that this is the origin of the surplus voltage, also in the case of the zinc CC, which will be discussed below.

The liquid junction potential arises when ions with different charges diffuse at different speed: the fastest ions accumulate at the forefront of the diffusion interface and leave the opposite charges on the rearward. The net charge distribution generates a voltage. In terms of kinetics, the diffusion of Zn^{++} ions through the liquid junction (from the concentrated solution to the diluted one) corresponds to a current which has an opposite direction with respect to the current that is generated when the cell is connected to the load. Hence, the contribution of zinc ions is detrimental to the power production. On the contrary, the diffusion current of Cl^- ions has the same direction as the cell current, so the chlorine contribution to the power production is beneficial. In this sense can be interpreted the beneficial use of a membrane which is only permeable to Cl^- ions, and the usual reduction of the performances when the simple CC is used.

However, the real situation for ZnCl_2 solutions is completely different, because zinc mainly diffuses through the junction in the form of negatively charged complexes, such as ZnCl_3^- and ZnCl_4^{--} :¹⁹ also zinc thus generates a beneficial diffusion current, i.e., with the same sign as the cell current. Roughly speaking, the diffusion of zinc mainly takes place in the form of undissociated ZnCl_2 molecules which also drag Cl^- ions with them, against the electrostatic force; in other words, the diffusion of zinc pumps additional Cl^- ions uphill, thus converting the free energy (which drives diffusion) into electric energy.

In quantitative terms, the voltage of the CC is^{20–22}

$$\Delta V_{\text{Zn}} = \frac{\mu_{\text{Zn}^{++}}(c_H)}{2N_A e} - \frac{\mu_{\text{Zn}^{++}}(c_L)}{2N_A e} - \sum_j t_j \frac{\mu_j(c_H) - \mu_j(c_L)}{z_j N_A e}, \quad (1)$$

where μ_j are the chemical potentials of the various species and t_j are the transference numbers (with the properties $0 < t_j < 1$ and $\sum_j t_j = 1$), which in general depend on the concentrations, but are assumed to be constant in the present simplified explanation. The three terms on the right side of the equation represent, respectively, the Nernst potentials on the two electrodes and the liquid junction potential.

It is easy to show that assuming the presence of only the ions Zn^{++} and Cl^- , we would obtain $0 < \Delta V_{\text{Zn}} < \Delta\mu/(2N_A e)$. The effective values of the transference numbers can however be significantly altered (and even become negative) when complexes are formed in the solution. This can be understood by recalling that the transference number, for a homogeneous solution in the presence of an electric field, can be defined as $t_j = \Phi_j z_j e / I$, where Φ_j is the flow of the j th ion and I is the total current. In our case, taking into account the presence of the complex ZnCl_3^- (other complexes are here neglected for simplicity), we have $t_{\text{Zn}^{++}} = 2e\Phi_{\text{Zn}^{++}}/I$, $t_{\text{Cl}^-} = -e\Phi_{\text{Cl}^-}/I$, and $t_{\text{ZnCl}_3^-} = -e\Phi_{\text{ZnCl}_3^-}/I$. But, neglecting the distinction between isolated ions and complexes, the total (or “apparent”) fluxes of zinc and chlorine are $\Phi_{\text{Zn}^{++}} = \Phi_{\text{Zn}^{++}} + \Phi_{\text{ZnCl}_3^-}$ and $\Phi_{\text{Cl}^-} = \Phi_{\text{Cl}^-} + 3\Phi_{\text{ZnCl}_3^-}$, respectively. As a result, we obtain the “apparent” transference numbers $\tilde{t}_{\text{Zn}} = 2e\Phi_{\text{Zn}^{++}}/I = t_{\text{Zn}^{++}} - 2t_{\text{ZnCl}_3^-}$ and $\tilde{t}_{\text{Cl}} = -e\Phi_{\text{Cl}^-}/I = t_{\text{Cl}^-} + 3t_{\text{ZnCl}_3^-}$, representing the transference of the zinc and chlorine atoms irrespectively of the molecule they belong to.

At equilibrium, $\mu_{\text{ZnCl}_3^-} = \mu_{\text{Zn}^{++}} + 3\mu_{\text{Cl}^-}$. This allows us to rewrite Eq. (1) as

$$\Delta V_{\text{Zn}} = \frac{\Delta\mu}{2N_A e} [1 - \tilde{t}_{\text{Zn}}], \quad (2)$$

in which only the apparent transference number of zinc shows up. The experiments^{19,23} show that Zn^{++} presents a negative apparent transference number $\tilde{t}_{\text{Zn}} = -0.52$ at 80% concentration, which justifies the observed voltage exceeding by more than 50% the reversible voltage. This negative transference number can be explained assuming that the solution contains negatively charged complexes containing zinc, such as the above-mentioned ZnCl_3^- , possessing a high mobility.

The CC for power production we studies has two 30 mm-diameter, 0.1 mm-thick zinc foils (supplied by Alfa Aesar) as electrodes, spaced by 4 mm, with a filter paper between them as diaphragm (see the sketch in Fig. 1(b)). We fluxed $0.5 \text{ cm}^3/\text{s}$ of solutions at concentrations $c_L = 0.05$ and $c_H = 0.8$ (expressed as the ratio between the mass of the solute with respect to the total mass of the solution) on the two sides of the diaphragm.

The measured voltage as a function of the current is reported in Fig. 3(a). It can be noticed that the CC voltage ΔV_{Zn} is more than 1.5 times larger than ΔV_{rev} in open-circuit and remains larger up to a current of 20 A/m^2 . The higher voltage generated by the CC is one of the main reasons for its excellent performances.

Figure 3(b) reports the produced power: it reaches a maximum of 3.7 W per square meter of electrode, at a current of 26 A/m^2 . The overvoltage is nearly linear in the current, corresponding to an equivalent series resistance of $5.7 \text{ m}\Omega$ for a cell of 1 m^2 . The main contribution comes from the transport inside the solution, which decreases with the increase of the concentration down to 7 mS/cm at 80%.

The cost of the zinc chloride CC for power production could be less than 0.5 euro/W , assuming that the main cost comes from the 0.1 mm -thick zinc foils used as electrodes. Better performances can easily be obtained by reducing the distance between the electrodes; however, the cost per W ratio that we estimate with our proof-of-principle is already by far the best result in terms of cost per power among the SGP devices: for example, the membranes used for reverse

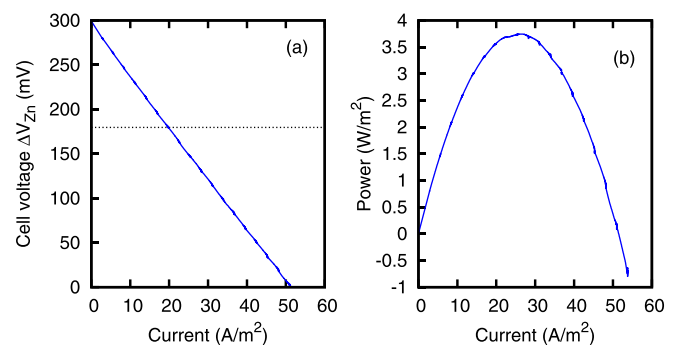


FIG. 3. Experiments with the concentration cell with ZnCl_2 solutions at 5% and 80% and Zn electrodes, under a current flow. Panel (a): cell voltage ΔV_{Zn} ; the horizontal line is the voltage ΔV_{AccMix} of the AccMix device with the same concentrations. Panel (b): produced power.

electrodialysis produce a power of the order of 10 W/m^2 with a cost of the order of 100 euro/m^2 .

The reported results show that the complex-forming solutions can be exploited for realizing a very effective SGP device, particularly suitable for the production of electrical current from low-temperature heat sources.⁷ Further improvements might be hopefully obtained with nanostructured electrodes, or with suitably chosen solutes that form complexes: as a guide for the selection of the latter, the relevant characteristics are the presence of a strongly negative transference number of the ion which is captured by the electrodes, which gives a high cell voltage, and a high boiling point elevation, which ensures a high efficiency of the overall process, when the device is coupled to a distiller for performing the thermo-electric conversion.

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