P H Y S I C A L   R E V I E W   L E T T E R S

Extracting Renewable Energy from a Salinity Difference Using a Capacitor

Doriano Brogioli

Dipartimento di Medicina Sperimentale, Università degli Studi di Milano-Bicocca, Via Cadore 48, 20052 Monza, Italy
(Received 10 April 2009; published 29 July 2009)

Completely renewable energy can be produced by using water solutions of different salinity, like river water and sea water. Many different methods are already known, but development is still at prototype stage. Here I report a novel method, based on electric double-layer capacitor technology. Two porous electrodes, immersed in the salt solution, constitute a capacitor. It is first charged, then the salt solution is brought into contact with fresh water. The electrostatic energy increases as the salt concentration of the solution is reduced due to diffusion. This device can be used to turn sources of salinity difference into completely renewable sources of energy. An experimental demonstration is given, and performances and possible improvements are discussed.

A massive dissipation of free energy takes place at the estuary of rivers: fresh and salt water mix, giving rise to the less ordered state constituted by water of uniform salinity, thus dissipating about 2.2 kJ of free energy per liter of fresh water dispersed into the sea [1]. Since the 1970s, it has been recognized that it is possible to interpose a suitable device between the flow of fresh water and the salt water, in order to exploit the free energy connected with the salinity difference as a completely renewable energy source. Already described techniques are pressure-retarded osmosis [2,3], based on semipermeable membranes, reverse electrodialysis [4], based on ion selective membranes, concentration electrochemical cells [5], devices exploiting difference in vapor pressure [6]. Such devices generate a power of the order of 1 kW with a fresh water flow of 1 l/s.

Recently this energy source received renewed interest [7,8], leading to the development of prototype plants [9]. High membrane cost and short life due to fouling are the main problems that prevented a large-scale utilization of membrane-based techniques, while the vapor pressure method relies on a very small pressure difference, and its application is quite challenging [8]. Here I propose a novel method that can make practical applications feasible, based on electric double-layer (EDL) capacitor technology [10,11]. The EDL capacitor is constituted by activated carbon electrodes immersed in sea water. It stores the charge in the EDLs constituted by counter ion distributions close to the electrode surfaces [12]. Following the method here proposed, the salt solution is then brought into contact with fresh water. Salt ions diffuse away from the electrodes, against the electrostatic force: the electrostatic energy of the whole system increases. I show experimental evidence of this energy increase, and that the surplus energy can be extract from the capacitor, thus converting the salinity difference into usable power. Extrapolation from the experimental apparatus to a real working device suggests that this method can produce a power of the same order of membrane-based methods.

An analogy can help to describe the physical principle of the method. Consider an electrostatic capacitor, made of two conductive plates with a solid dielectric medium in between, which can be inserted or extracted. When the plates constituting the capacitor are charged, the electrostatic force attracts and keeps the dielectric medium inside the capacitor. The work done to extract the dielectric is converted into electrostatic energy, appearing as an increase of voltage between the plates, while the accumulated charge remains constant. This kind of device is thus able to transform mechanical work into electrostatic energy.

The dielectric medium of the capacitor described in this Letter is substituted by salt water. After the capacitor has been charged, the solution is brought into contact with fresh water, so that salt ions diffuse away from the capacitor. I will show that, in analogy with the previous case, the ion removal, performed by diffusion, increases the voltage between the plates, at the expense of free energy of the two solutions involved in the process, namely, salt and fresh water.

Figure 1 shows the device used to experiment the above described physical principle. The cell contains two electrodes, and is filled with the changeable solution. Two water reservoirs, with two solutions at different NaCl concentration representing salt and fresh water, are connected to the cell by means of pumps, which are activated in sequence, so that the concentration of the solution in the cell can be changed from a low concentration to a high concentration and *vice versa*. The electrodes are made of activated carbon, an extremely porous conductor, shaped in 2 mm-diameter disks, 0.1 mm thick. A switch can temporarily connect the electrodes to a charge or a discharge circuit. The load is represented by the resistor $R = 1$ kΩ, through which charge and discharge currents flow.

The two electrodes immersed in the solution constitute a capacitor. When a current flows through the capacitor, each electrode repels ions of same charge, and attracts ions of opposite charge, thus forming an oppositely charged ionic
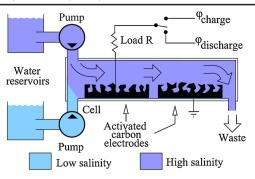
FIG. 1 (color online).   Schematic view of the device. The cell contains two electrodes, made of porous activated carbon, constituting a capacitor, which can be charged and discharged. The cell is filled with a NaCl solution, coming from one of the reservoirs.

layer, close to its surface: charge is actually stored in the resulting EDL. Electrons do not flow between the electrode and the solution, because the capacitor is operated at a voltage lower than the electrolytic potential of the ions in solution. For water solutions, this "breakdown voltage" is about 1 V; above this value, current flow due to redox chemical reactions quickly discharges the EDL.

The device here described shares the use of activated carbon with the so-called EDL capacitors, components actually used for electronic devices [10,11], since this extremely porous and conducting material features a vary large surface, resulting in a huge capacitance. The material used in this work is a commercial steam activated lignite coal, Norit Darco 12×20 (provided by Sigma-Aldrich). The properties, as measured and declared by the producer, are: iodine number 625 mg/g; specific surface area (BET, nitrogen adsorption) 650 m^2/g; tannin value: 150 mg/l; methylene blue adsorption: 160 mg/g; molasses decolorizing efficiency 85%; apparent density: 0.38 g/cm^3; total pore volume 0.95 cm^3/g; resistivity: 0.9 Ω cm.

The device described in this Letter bears analogies also with the "capacitive desalination" devices [13], in which electric energy is consumed, in order to remove salt ions from sea water. Actually, the process reported here can be thought of as the reverse of capacitive desalination, in the same way as pressure-retarded osmosis [3], reverse electrodialysis [4] and vapor pressure method [6] are the counterparts of desalination methods, namely, reverse osmosis, electrodialysis, and vacuum distillation.

The graph in Fig. 2(a) has been obtained by charging the capacitor with known amounts of charge Q and measuring the resulting voltage $\varphi(Q)$, at different concentrations of salt in water. EDLs are currently described by Gouy-Chapman-Stern theory [12], but a quantitative comparison of theory with results of Fig. 2(a) is not trivial, due to the porous structure of the electrodes (see for instance Ref. [14]), and is beyond the scope of this Letter; instead, a brief qualitative explanation of the theory is given.

Gouy-Chapman-Stern theory models the ion distribution close to planar electrodes as the sum of an adsorbed EDL
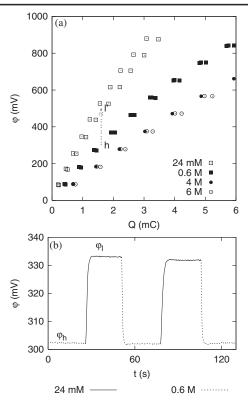

FIG. 2.   Relation between accumulated charge Q and voltage $\varphi(Q)$ across the electrodes. (a) Measured graph of $\varphi(Q)$, for different concentration of salt in water. The concentration dependence is explained in terms of change in EDL thickness. (b) Graph of the open-circuit voltage, as the solution is changed from 0.6M to 24 mM and *vice versa*.

(Stern EDL) and a diffuse EDL. Ions in the diffuse EDL reach an equilibrium between diffusion, which tends to equalize the ion concentration, and electrostatic force, that, on the contrary, tends to increase the charge imbalance close to the surface. This equilibrium is described by Poisson-Boltzmann equation, and the Gouy-Chapman solution for ion concentrations and potential can be obtained analytically [12]. At long distance from the electrode the charge is completely screened, so that the electric field is present only inside the diffuse EDL. The relation between the surface charge density σ and the potential difference φ between the electrode and the bulk solution is

$$\varphi = \frac{2k_B T}{e} \sinh^{-1}\left(\frac{\sigma}{\sqrt{8 C N_A \epsilon_0 \epsilon_r k_B T}}\right), \qquad (1)$$

where K_B is the Boltzmann constant, T is the temperature, e is the electron charge, N_A is the Avogadro constant, ϵ_0 is the electric constant, ϵ_r is the relative dielectric constant, and C is the concentration; the equation is valid for a symmetric, monovalent electrolyte as NaCl.

Equation (1) shows that a decrease of concentration C leads to an increase of potential. In order to better explain this fact, I rewrite Eq. (1) in terms of EDL effective thickness L, implicitly defined so that $\varphi = L\sigma/(\epsilon_0 \epsilon_r)$,

$$L = \lambda_S \sinh^{-1}\left(\sqrt{\frac{\chi}{C}}\right), \qquad (2)$$

where $\lambda_S = 2K_BT\epsilon_0\epsilon_r/(e\sigma)$ and $\chi = \sigma^2/(8N_A\epsilon_0\epsilon_rK_BT)$. For a given concentration, the EDL thickness L reflects the equilibrium between electrostatic forces and diffusion. In a less concentrated solution the EDL is thicker, since the solution is less effective in screening the charge, so that the electric field can extend on a longer distance. When the concentration of the solution is changed, the ions move towards the new equilibrium distribution. In the case of concentration reduction, in which L increases, ions actually move against electrostatic forces, driven by diffusion.

The behavior of ion solution inside a porous material is much more complex [15]. For what concerns concentration dependence, Eq. (1) holds for pores with diameter much bigger than L. In the opposite situation, the pore is too small to contain the diffuse EDL, and capacity is reduced with respect to the planar case [16]. This effect enhances the reaction of the system to concentration changes, when L changes across the pore diameter, and must be considered when engineering the porous structures in order to improve the performances of energy production with the present device. Other effects that must be considered include adsorption, which generates Stern EDL, and the functionalization of the surface, giving pseudocapacitance.

From Fig. 2(a), the capacitance can be evaluated: it is about 2.8 mF at $[NaCl] = 24$ mM, 5.0 mF at $[NaCl] = 0.6M$, and 8 mF at $[NaCl] = 6M$. The measured internal resistance is respectively 3 kΩ, 800 Ω and 500 Ω, quite high and mainly due to the large separation between electrodes.

Point h in Fig. 2(a) describes the cell filled with $[NaCl] = 0.6M$, representing sea water, with the electrodes charged at $\varphi_h = 300$ mV. When the solution initially present is substituted with a solution at lower concentration $[NaCl] = 24$ mM, representing fresh water, the charge should remain unchanged, while the potential should rise up to the value $\varphi_{l'} = 500$ mV: the system goes from point h to point l'.

This effect is experimentally shown in Fig. 2(b), where the open-circuit potential across the capacitor terminals is plotted, as a function of time. With $[NaCl] = 0.6M$, the capacitor is charged at $\varphi_h = 300$ mV. After disconnecting the capacitor from charge circuit, the solution is repeatedly substituted, alternating $[NaCl] = 24$ mM and $[NaCl] = 0.6M$. Correspondingly, the potential goes from $\varphi_h = 300$ mV to $\varphi_l = 333$ mV, and *vice versa*. The actual value $\varphi_l = 333$ mV is much less than $\varphi_{l'}$; this fact is likely due to a partial and temporary trapping of a fraction of salt ions inside the porous electrodes, due to slowing of diffusion.

In order to extract energy from the capacitor, a cycle with four phases is performed, as shown in Fig. 3(a). Voltage across the electrodes of the capacitor and current flowing through the load R are shown in Fig. 3(b).

Phase A: The cell is filled with salt water. The capacitor is charged, through R, towards voltage $\varphi_{charge} = 300$ mV.
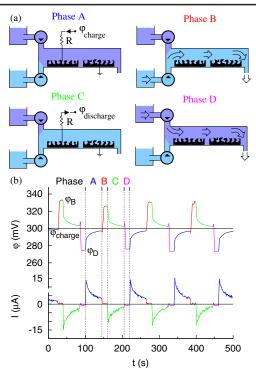

FIG. 3 (color online). Cycle for extracting energy from salinity difference. (a) Scheme of the four phases of the cycle. (b) Graph of the voltage φ across the capacitor electrodes and of the current I flowing through the load R, along the cycles.

Phase B: The circuit is open. The cell is flushed with fresh water: the voltage increases up to $\varphi_B = 333$ mV.

Phase C: The capacitor is discharged, through R, towards voltage $\varphi_{discharge} = 300$ mV. It is evident a sudden voltage drop, due to internal resistance in the capacitor, followed by a nearly exponential decay.

Phase D: The circuit is open. The porous electrodes are brought into contact with salt water. The voltage decreases down to $\varphi_D = 274$ mV.

In both phases A and C, current flows through R: the device supplies power to the load, *quod erat demonstrandum*, at a rate of about 5 μJ per cycle. On the other hand, I will show that the total incoming charge, that is, the integral of the current, is close to 0 C: the charge and discharge circuit provides no net energy, so that the energy dissipated by R completely comes from salinity difference.

A single cycle is represented in Fig. 4 in the plane φ versus Q. This representation is particularly useful, since the energy gained along the cycle equals the area of the enclosed surface. This shows a close analogy with the cycles of thermal engines used to extract energy from temperature differences, where potential-charge graph is replaced with pressure-volume graph. In analogy with thermal engines, phases A,B,C, and D correspond to compression, heating, expansion, and cooling.

The evaluation of the integral of the current is critical, since even a small charge loss of 33 μC corresponds to the whole produced energy. The charge loss is due to the
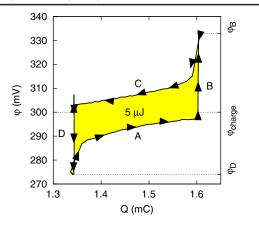
FIG. 4 (color online). Representation of the cycle on the potential *versus* charge graph. The area represents the extracted energy: in this case, it is 5 μJ.

leakage current of the capacitor. Care has been taken to evaluate this loss, in order to compare it with the energy gained by salinity difference. In order to evaluate the self-discharge of the capacitor, it has been charged at $\varphi = 300$ mV, and then the voltage across the isolated electrodes has been measured over time. In the $[NaCl] = 0.6M$ solution (in which leakage is higher), the voltage decreases roughly uniformly, with a total decrease of $\delta\varphi = 1.6$ mV over $\Delta t = 6$ minutes. The leakage current is $I = C\delta\varphi/\Delta t$, about 22 nA. The energy lost due to leakage current, along a cycle lasting $T = 120$ s, is thus around $T\varphi I/2 \approx 400$ nJ, about one tenth of the extracted energy.

By a calculation based on the graph in Fig. 4, it can be noticed that the energy generated by the salinity difference is about 10 μJ, but half of that energy is dissipated by the internal resistance of the capacitor.

The experiment shows the feasibility of the idea, and allows to forecast the power outcome of an industrial-scale device. The experimental device gives 5 μJ per cycle, equivalent to 2.2% of the energy it stores. The best materials developed for EDL capacitors reach a specific capacitance of the order of 300 F/g [10], corresponding to an energy density in aqueous electrolyte of about 37 J/g: the expected energy production is of the order of 1.6 kJ/kg per cycle. At each cycle, the quantity of fresh water that must substitute the salt water in the pores of the electrode is a fraction of the volume, so a power of the order of 1.6 kJ per liter of fresh water can be reached, which is of the same order of membrane-based methods.

A cycle rate of the order of 1 Hz can be reached, leading to a power production of the same order of membrane-based methods. The most time-expensive operation is the solution change, which is not needed in membrane-based and represents the main drawback of the present method. It can be performed in a fraction of a second, by placing the electrodes on the walls of small channels, in which the liquids are injected in rapid succession. Charge and dis-

charge times do not represent an issue, since time constants of the order of 0.1 s are often reported, and commercial devices featuring time constants down to 1 ms are available [17]. It is not necessary that the liquids flow *between* the electrodes: in order to obtain a low internal resistance, along with hydraulic accessibility, the electrodes can be deposited on a thin spacer immersed in the liquid, or printed as closely spaced stripes [18].

Losses due to electric leakage can be neglected, since commercial devices have a self-discharge time constant at least of the order of days. Power lost for pumping must be taken into account. In order to evaluate this pumping power, I consider electrodes 100 μm thick, constituting 1 mm-diameter channels, 10 cm long; the inside volume is exchanged each second. By using the Poiseuille equation, I evaluate a pumping power of the order of 40 W per Kg of activated carbon, which is less than the extracted energy.

The described technique is thus competitive with membrane-based methods. Performances will be further improved by suitably engineering the structure of the porous electrode material.

[1] R. W. Norman, Science **186**, 350 (1974).
[2] O. Levenspiel and N. de Vevers, Science **183**, 157 (1974).
[3] S. Loeb, Science **189**, 654 (1975).
[4] J. N. Weinstein and F. B. Leitz, Science **191**, 557 (1976).
[5] F. E. Kiviat, Science **194**, 719 (1976).
[6] M. Olsson, G. L. Wick, and J. D. Isaacs, Science **206**, 452 (1979).
[7] J. W. Post, J. Veerman, H. V. M. Hamelers, G. J. W. Euverink, S. J. Metz, K. Nymeijer, and C. J. N. Buisman, J. Membr. Sci. **288**, 218 (2007).
[8] A. T. Jones and W. Finley, in *Oceans 2003* (2003), Vol. 4, p. 2284.
[9] K. Gerstandt, K. V. Peinemann, S. E. Skilhagen, T. Thorsen, and T. Holt, Desalination **224**, 64 (2008).
[10] P. Simon and Y. Gogotsi, Nature Mater. **7**, 845 (2008).
[11] A. S. Aricò, P. Bruce, B. Scrosati, J. Tarascon, and W. van Schalkwijk, Nature Mater. **4**, 366 (2005).
[12] R. J. Hunter, *Foundation of Colloid Science* (Clarendon Press, Oxford, 1993), Chap. 6, p. 316.
[13] Y. Oren, Desalination **228**, 10 (2008).
[14] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, Science **313**, 1760 (2006).
[15] J. S. Huang, B. G. Sumpter, and V. Meunier, Angew. Chem., Int. Ed. **47**, 520 (2008).
[16] C. M. Schaldach, W. L. Bourcier, P. H. Paul, and W. D. Wilson, J. Colloid Interface Sci. **275**, 601 (2004).
[17] Supercapacitor produced by NEC/TOKIN, High capacity, low ESR type, catalog number HPSN0G473ZL, about 1 ms time constant.
[18] M. Kaempgen, C. K. Chan, J. Ma, Y. Cui, and G. Gruner, Nano Lett. **9**, 1872 (2009).