



Modification of the surface of activated carbon electrodes for capacitive mixing energy extraction from salinity differences



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ARTICLE INFO

Article history:

Received 25 July 2014

Accepted 31 August 2014

Available online 16 September 2014

Keywords:

Energy from salinity difference

Surface groups

Capacitive mixing

Electric double layer

Gouy–Chapman–Stern model

ABSTRACT

The “capacitive mixing” (CAPMIX) is one of the techniques aimed at the extraction of energy from the salinity difference between sea and rivers. It is based on the rise of the voltage between two electrodes, taking place when the salt concentration of the solution in which they are dipped is changed. We study the rise of the potential of activated carbon electrodes in NaCl solutions, as a function of their charging state. We evaluate the effect of the modification of the materials obtained by adsorption of charged molecules. We observe a displacement of the potential at which the potential rise vanishes, as predicted by the electric double layer theories. Moreover, we observe a saturation of the potential rise at high charging states, to a value that is nearly independent of the analyzed material. This saturation represents the most relevant element that determines the performances of the CAPMIX cell under study; we attribute it to a kinetic effect.

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1. Introduction

Naturally occurring salinity differences can be used for generating completely clean and renewable energy [1–3]. For example, each liter of river water dispersed into the sea corresponds to a free energy loss of around 2.3 kJ, and a significant fraction of this energy could be intercepted and converted into electrical energy. Considering all the rivers, the global potential of this source of energy is around 1 TW [4], a relevant fraction of the whole energy demand. Brines can also be locally available: for example, salt lakes (e.g. Dead Sea) [5], coal-mine brines [6] produced by dissolving geological deposits, or salterns [7]. They can be used vs. sea water, thus avoiding the fresh water consumption.

The key point of the above described processes is the conversion of the salinity difference into electrical current. Known techniques include pressure-retarded osmosis (PRO) [8–10] and reverse electrodialysis (RED) [11,12]. In PRO, a semi-permeable membrane is interposed between salt and fresh water, generating

an osmotic water flow that is fed to a turbine. In RED, the membranes are permeable to either positive or negative ions; the ion diffusion across them constitutes a current that can be extracted.

A new technique, called “capacitive mixing” (CAPMIX) has been recently introduced [13–17]. This technique performs the mixing process of the two solutions in a controlled way, by means of the CAPMIX cycle sketched in Fig. 1a. A cell contains a couple of electrodes, dipped into the ionic solution. The cycle begins with the cell filled with the high-salinity solution. The four steps are as follows:

- A The cell is charged by means of an external device.
- B The circuit is opened. The solution in the cell is substituted with the low-salinity feed solution.
- C The cell is discharged through a load; the electrical current flows in the opposite direction with respect to step A.
- D The circuit is opened. The liquid in the cell is substituted with the high-salinity feed solution.

Fig. 1b shows the voltage vs. charge graph for this cycle. During step A the cell voltage increases, and an electrical charge is temporarily stored in the electrodes. The solution change that takes place in step B, in open circuit, induces a cell voltage rise ΔV . The stored charge is recovered in step C, at a higher voltage with respect to step A. For this reason, due to the voltage rise, the curve encloses an area, which represents the extracted energy.

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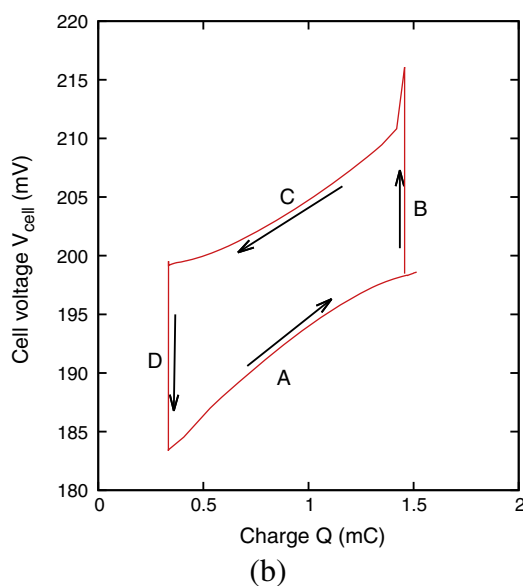
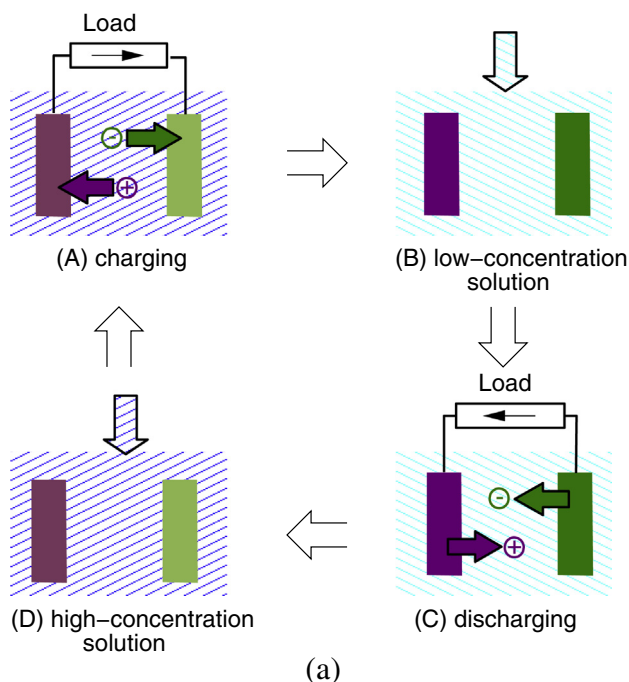


Fig. 1. The CAPMIX cycle. Panel a: sketch of the cycle. Panel b: representation of the cycle in the voltage vs. charge graph. The phases are: A, charging; B, flow of low-salinity solution; C, discharging; D, flow of high-salinity solution.

During step A, the ions coming from the solution at higher salinity are temporarily stored into the electrodes, and they are later released into the solution at lower salinity during step C, thus decreasing the total salinity difference. This process can be described as a capacitor-mediated mixing, hence the name “capacitive mixing”. It is thus evident that the energy is extracted at the expense of the free energy of the solutions; indeed, it has been shown that the voltage rise is connected with the ability of the electrodes to store the salt inside them, when they are charged during phase A [18].

The key element of the CAPMIX technique is the voltage rise that takes place when the solution concentration is changed: indeed, the produced power is roughly proportional to the square of the voltage rise, by assuming a fixed internal resistance. Various techniques, based on different physical principles and making use

of different types of electrodes, have been proposed for obtaining the voltage rise:

Capacitive double layer expansion (CDLE) makes use of microporous (typically, activated carbon) electrodes [19–21]. The voltage rise is due to the variation of the thickness of the electric double layer that forms on the internal surface of the porous electrodes.

Capacitive Donnan potential (CDP) makes use of assemblies, each composed by an activated carbon electrode covered with a perm-selective membrane [22–26]. The voltage rise is due to the variation of the Donnan potential across the membrane.

Battery-like electrodes make use of materials that capture the ions in the solution by means of redox reactions [27–30]. The voltage of the electrodes with respect to the solution reflects the chemical potential of the ions in the solution, that changes according to the variation of their activity; this originates the voltage rise.

In the seminal work [13], the electric double layers necessary for the CDLE technique were created by electrically charging the electrodes by means of an external power supply. Unfortunately, the self-discharge of the activated carbon led to the necessity of continuously charging the electrodes, thus losing an amount of power that was comparable with the produced power. For this reason, experimental and theoretical investigations have been carried out [31,32] about the possibility of “chemically” charging the electrodes, so as to produce on their surface an electric double layer without the need of an external power supply, and so without undergoing the self-discharge phenomenon. A similar chemical charging has been already studied in the context of capacitive deionization [33].

In this paper, we present results on the open-circuit potentials, either in high- or low-salinity solutions, of activated carbon electrodes that are chemically charged by adsorption or chemical binding of charged molecules on their surface, obtained by means of suitable specific treatments. In Section 2 we describe the experimental methods and the preparation of the samples, while in Section 3 we present the experimental results. We show that the modification with charged molecules changes the potential rise of the electrodes, and allows us to produce couples of electrodes with improved voltage rise.

In order to shed light on the physical processes lying behind the observed behavior, we also study the relationship between the potential rise and the base potential, i.e. the potential of the electrode in the high salinity solution, as determined by the electrode’s charging status. Various models predict [31] that the potential rise saturates to a constant positive (negative) value for increasing (decreasing) base potential, with a transition between the two at intermediate potentials. Our experimental results show that, in all the samples, it is possible to observe at least one of the two saturations (either at high or low potentials) in the range of base potentials that is accessible by experiments; moreover, a part of the transition zone is also visible. In Section 4 we discuss the results and propose qualitative explanations.

2. Materials and methods

2.1. Experimental setup

Fig. 2a shows the experimental setup. The liquid in the cell can be switched between two solutions at different concentrations. The voltages of the two activated carbon electrodes with respect to the reference electrode are monitored; the resulting potentials are called $\varphi(t)$ and $\varphi_C(t)$, respectively for the working and counter electrodes (arbitrarily chosen). In the work presented in this paper,

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