Electrochimica Acta 92 (2013) 304–314

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electro-diffusion of ions in porous electrodes for capacitive extraction of renewable energy from salinity differences

Raúl A. Rica[a,*], Roberto Ziano[a], Domenico Salerno[a], Francesco Mantegazza[a], Martin Z. Bazant[b,c], Doriano Brogioli[a]

[a] Università di Milano-Bicocca, Via Cadore 48, 20052 Monza, Italy
[b] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[c] Department of Mathematics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

ARTICLE INFO

Article history:
Received 5 October 2012
Received in revised form 7 January 2013
Accepted 11 January 2013
Available online 20 January 2013

Keywords:
Salinity differences
Porous electrodes
Super-capacitors
Electrodiffusion
Renewable energy

ABSTRACT

One dimensional theory of the electro-diffusion of ions in activated carbon porous electrodes is applied to describe the dynamic cycle of the capacitive mixing (CAPMIX) based on the double layer expansion (CDLE) technique to harvest renewable energy from salinity gradients. The model combines the electro-diffusion of ions with adsorption and desorption of charge and neutral salt into the double layers at the solid liquid interface, providing a comprehensive and accurate description of the full CAPMIX cycle experimentally measured in prototype cells. A careful analysis of the simulated cycles identifies key parameters for the optimization of the extracted power, like the appropriate thickness and micro-structure of the electrodes, best materials and operation conditions of the electrochemical cell. These directions will be fundamental in the development of this technique as an economically competitive renewable energy source.

1. Introduction

It is well known that clean, renewable energy can be extracted from the controlled mixing of waters with different salinities [1–7]. Several approaches have been developed to efficiently harvest the so-called "Blue Energy", a resource that could be able to globally produce up to 2 TW from the natural mixing of waters occurring in the rivers flowing into the sea [8–10]. Pressure retarded osmosis (PRO) [11–13] utilizes the osmotic pressure difference that develops when a semipermeable membrane (ideally, water-permeable, but salt-impermeable) separates two solutions of different concentration. This pressure difference is used to drive a flow of water from a dilute solution into a more concentrated one, which is converted into electrical power by a turbine and a pressure exchanger. In reverse electrodialysis (RED) [14–16], the two solutions with different salinities are brought into contact through an alternating series of anion and cation exchange membranes combined with two electrodes at each end. The chemical potential difference between salt and freshwater generates a voltage over each membrane and the total potential of the system is the sum of the potential differences over all membranes. These technologies make use of membranes, which are expensive to produce and easily get fouled and degraded. Moreover, they do not have infinitely high selectivity to the counterion and that they can discharge at high currents, losing selectivity [17].

A novel technique based on the use of electric double layer (EDL) electrochemical capacitors [18–20] has been recently proposed by Brogioli [21], leading to the family of technologies that we now call "capacitive mixing" (CAPMIX) [8]. In CAPMIX, the generation of energy is directly linked to the mixing process, so there is no need for intermediate processes nor conversions, simplifying its implementation and up-scaling. The electrodes of EDL super-capacitors are made of porous activated carbon particles, which are cheap to produce and have long lifetimes. Considering these advantages with respect to other approaches, this technique appears to be a promising way to harvest renewable energy at competitive cost, to be added to the pursued mix of energy sources. Fouling is also an issue in porous electrodes, and much work has to be done in order to minimize its impact. In general, fouling by chemical and biological agents will depend on the local chemistry and biology of rivers, and existing methods to clean membranes and avoid their fast degradation [22] are expected to be also applicable to the maintenance of porous electrodes.

The strategy originally proposed by Brogioli [21,23], called "capacitive energy extraction based on double layer expansion" (CDLE), does not need any membrane, but is based on the dependence of the capacitance of the EDL on the salt concentration. "Capacitive energy extraction based on Donnan potential" (CDP)

---

* Corresponding author.
E-mail address: rul@ugr.es (R.A. Rica).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.01.063

combines the CDLE strategy with elements of RED [24,25], incorporating ion-selective membranes to a capacitive cell for charge storage. The inclusion of membranes avoids the need to externally charge the capacitive cell, but adds the aforementioned drawbacks they present. Other recent approaches include the use of ion-selective nanopores to induce current between reservoirs with different salt concentrations [26], useful for portable energy generation devices; or the "mixing entropy battery" (MEB) [27], which is able to extract and store electrochemical energy by selective interactions (faradaic reactions) of their electrodes with ions in solution. MEB does not store charge capacitively, but pseudo-capacitively as chemical energy inside the electrode bulk crystal structure, and uses the dependence of the Nernst potential on salt concentration. Therefore, MEB is in fact a "pseudo-CAPMIX" technique, since the device acts like a "pseudo-capacitor".

CAPMIX is strongly related to capacitive deionization (CDI) [28,29], a technique that consumes energy to capacitively charge pairs of porous electrodes, thus removing ions from the electrolyte between them. They are not only inverse processes, but it has been shown that, ideally, they can be operated reversibly in order to be thermodynamically equivalent [30,31] and that the same design improvements could lead to optimal performance of both techniques [32].

Although significant advances in the performance of CAPMIX cells have been achieved with simplified models [23,25], an appropriate optimization can be developed only if a full comprehension of all the involved mechanisms is available. Up to now, the bottleneck of CDLE has been the unavoidable presence of charge leakage, i.e., the loss of the stored charge due to undesired surface reactions, that limits the maximum power production [23,25]. We have recently shown that leakage can be almost completely avoided [33], but the development of a competitive technology still requires further advances on the understanding of the properties of the solid/liquid interface, in particular the mechanism responsible for the leakage itself, and guidelines for optimal cell design and operation. Indeed, like in other supercapacitor technologies [18,34,35], the transport of ions inside the porous matrix strongly influences the performance of a CAPMIX cell [36], which has to be taken into account.

Despite the fact that the physical origin of the EDL is easy to understand, its rigorous modeling is far from simple, even in equilibrium conditions [37]. Recent approaches have analyzed the thermodynamic CAPMIX cycle, aiming at the maximization of the extracted energy. The numerical analysis of a modified Poisson–Boltzmann free-energy density functional performed by Boon and van Roij [31] proposes a more efficient cycle than the one tested by Brogioli. More elaborate treatments solve the full set of electrokinetic equations inside a cylindrical pore or use a cell model to describe the EDLs in a highly concentrated plug of carbon particles [38,39]. It is also worthwhile to mention that a continuum description of EDL is not strictly valid inside micropores of size comparable to those of hydrated ions, as confinement effects can lead to very large capacitances inside sub-nanometer micropores [40,41], capacitance oscillations for decreasing pore size [42–44] or different charge storage mechanisms [45]. Moreover, steric effects are typically to be taken into account [46–50], specially under nano-confinement where there appear oscillations in charge density due to ion–ion ordering [51].

In this work, we aim at the description of the kinetics of the CAPMIX cycle, as other studies have previously addressed its thermodynamics. This kinetic description is essential in order to understand the unexpected behavior observed in experiments [21,23,36], and to improve present cell design and operation guidelines of a CAPMIX prototype. Therefore, we avoid a rigorous description of the EDLs and the transport therein, by using a macroscopic description of them. This description considers charge and salt adsorption into the EDLs as excess quantities that modify the electro-diffusion of ions in the macropores of the electrodes, where the solution is assumed to be electroneutral [52].

The paper is organized as follows. The CDLE principle and its application to Blue Energy harvesting is introduced in Section 2.1, followed by the description of voltage–charge and voltage–concentration relations of the EDL in Section 2.2. Then, the model is completed by the description of a 1D theory of electro-diffusion of ions (Section 2.3). After an overall description of the transport and adsorption phenomena in the porous electrodes (Section 3.1), we discuss some technical details aiming at the maximization of the extracted power from the CAPMIX cycle in Section 3.2.

2. Theory

2.1. The CDLE principle

Consider a parallel plate electrostatic capacitor. In such a device, the voltage difference between the two oppositely charged plates is directly proportional to their separation d according to $V = Q/C_s = Qd/\varepsilon$, Q being the charge per unit surface on each plate, C_s the specific (per unit surface) capacitance, and ε the electric permittivity of the medium between the plates. We can do work against the electrostatic force on this system by moving apart the two plates. The work thus done is stored by the capacitor as electrostatic energy, increasing the voltage difference between the two plates at constant charge.

As a first approach, the structure of the EDL that forms close to a charged surface in contact with an ionic solution can be thought of as a parallel plate capacitor, where one plate is the solid surface and the other one is the diffuse charge. A measure of the distance between the two plates is given by the Debye length λ_D, that depends on the bulk salt concentration C, as it is the result of a competition between the electrostatic forces that attract counterions to screen the surface charge with the diffusive force trying to equilibrate the concentration of all ionic species [37]. In the case of a monovalent electrolyte ($z_+ = -z_- = z = 1$, being $z_\pm$ the valence of cations and anions, respectively), the expression of the Debye length reads:

$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2Ce^2}} \tag{1}$$

ε_r being the relative electric permittivity of the liquid (typically water), ε_0 the electric permittivity of vacuum, k_B is the Boltzmann constant, T is absolute temperature, e is the electron charge and C is expressed in number of ions per unit volume. From this equation, it is clear that the EDL will be thicker the lower the salt concentration, and vice versa. The voltage drop in the diffuse part of the EDL ΔV_D can be described by the Gouy–Chapman surface charge–voltage relationship [37]:

$$\Delta V_D = 2V_T \sinh^{-1}\left(\frac{-Q}{2V_T(\varepsilon_r \varepsilon_0/\lambda_D)}\right) \simeq \frac{-Q\lambda_D}{\varepsilon_r \varepsilon_0} \tag{2}$$

where $V_T = k_B T/e$ is the thermal voltage and Q is the total charge per unit surface in the diffuse part of the EDL. The approximation stands for small surface charge, this limit clearly showing the similarity with a parallel plate capacitor. From Eqs. (1) and (2), we see that the voltage drop in the diffuse part of the double layer increases when C is decreased at constant Q.

By means of an electrochemical cell composed of two electrodes in an electrolyte solution of concentration C_{salt} externally charged with a battery V_{ext} (with an overvoltage close to zero), we can