



Polyelectrolyte-versus membrane-coated electrodes for energy production by capmix salinity exchange methods



M.M. Fernández ^a, R.M. Wagterveld ^b, S. Ahualli ^a, F. Liu ^b, A.V. Delgado ^{a, *}, H.V.M. Hamelers ^b

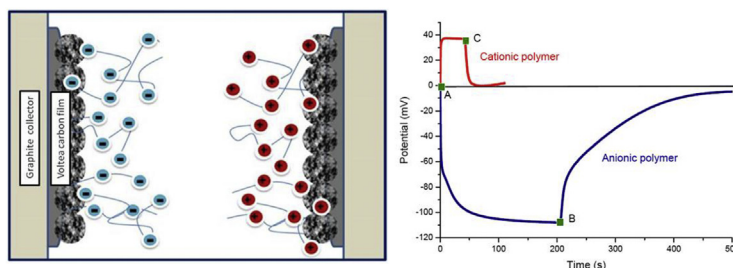
^a Department of Applied Physics, School of Sciences, University of Granada, 18071, Granada, Spain

^b WETSUS, Centre of Excellence for Sustainable Water Technology, 8900 CC, Leeuwarden, The Netherlands

HIGHLIGHTS

- Polyelectrolyte coated (“soft”) carbons for blue energy production are investigated.
- They are compared to membrane-coated electrodes (CDP).
- The energy per cycle is similar in both methods, but the kinetics is faster in CDP.
- Positively and negatively coated electrodes are investigated separately.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 July 2015

Received in revised form

30 September 2015

Accepted 23 October 2015

Available online 11 November 2015

Keywords:

Blue energy

Capmix techniques

CDP

Donnan potential

Polyelectrolyte coating

ABSTRACT

In this paper we analyze the energy and power achievable by means of a recently proposed salinity gradient technique for energy production. The method, denominated soft electrode or SE, is based on the potential difference that can be generated between two porous electrodes coated with cationic and anionic polyelectrolytes. It is related to the Capacitive Donnan Potential (CDP) technique, where the electrical potential variations are mostly related to the Donnan potential, of ion-selective membranes in the case of CDP, and of the polyelectrolyte coating in SE. It is found that although SE is comparable to CDP in terms of energy production, it presents slower rates of voltage change, and lower achieved power. The separate analysis of the response of positively and negatively coated electrodes shows that the latter produces most of the voltage rise and also of the response delay. These results, together with electrokinetic techniques, give an idea on how the two types of polyelectrolytes adsorb on the carbon surface and affect differently the diffusion layer. It is possible to suggest that the SE technique is a promising one, and it may overcome the drawbacks associated to the use of membranes in CDP.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Natural mixing of water streams with different salinities is an abundant but largely unused power source. However, since the

1950's [1], it has been recognized as a clean renewable energy resource available worldwide. The research to date tends to focus on the natural process of mixing river water with seawater in river mouths as the main source of salinity gradient (or blue) energy [2–4]. Within the recent past, other salinity difference sources have also grown in importance. Concentrated brine water from desalination plants can be paired with waste water from a treatment facility, reducing desalination energy cost [5]. The latest researches

* Corresponding author.

E-mail address: adelgado@ugr.es (A.V. Delgado).

have also led to a new interest in low temperature (<80 °C) waste heat and waste water from the industrial sector to convert it into useful work. For instance, waste heat can be used to generate low and high concentration solutions for salinity difference energy either by membrane distillation process [6] or by using thermolytic solutions [7]. In addition, small water temperature differences can be combined with salinity gradient for increased energy extraction by means of either thermal membrane properties [8] or changes in the capacitance of the electrical double layer [9]. As an interesting alternative, it has been recently shown that mixing solutions with different dissolved CO₂ concentrations is a related method which can be used to harvest energy from gas emissions [10,11].

A number of techniques have been developed to obtain the Gibbs free energy that is released when two electrolyte solutions of different concentrations are mixed. The most advanced approaches are the membrane-based PRO (pressure retarded osmosis) [12–14] and RED (reverse electrodialysis) [15,16]. They have different working principles, operating considerations and membrane properties [17,18]. PRO utilizes the osmotic pressure difference between two chambers to produce pressurized water to generate electricity through a hydro-turbine. In other words, the flow of water molecules (but not ions) into a more concentrated solution is the driving force of the technique. RED, on the other hand, uses membranes for the transport of ions and not water molecules. PRO and RED have been demonstrated at pilot scale [19,20] and are close to commercialization, although both still face some problems related to membrane performance and costs.

A recent approach, called capacitive mixing (capmix), comprises a group of techniques which are based on the variation of the potential difference between two porous electrodes by exchanging the ionic contents of the solution in contact with them [21,22]. An important difference with respect to the previous technologies is that here the two solutions do not flow simultaneously, but they flow alternatively through the same compartment which is a cell made of two oppositely faced activated carbon electrodes.

Two main techniques have been developed for the direct production of electrical energy based on this principle. In CDLE (capacitive double layer expansion method) the electrodes are charged with an external power supply in presence of a salty solution. When this is exchanged by fresh water, an increase of the cell potential is produced due to the associated decrease in the capacitance of the electrical double layer (EDL) [2,23–25]. Alternatively, in CDP (capacitive Donnan potential method) the voltage difference generation involves the use of ion selective membranes on each electrode, and the cell potential is controlled by the Donnan potential difference [3,26]. Improvements of the method have led to recently reported increases in the extracted power achieved [27,28]. In principle, the CDLE approach would be cheaper to produce and easier to implement due to absence of membranes, also associated to a lower internal resistance of the cell. However, problems with self-discharging have prevented a real advance of this technique [29,30]. In addition, physical, chemical and organic fouling inevitably associated to exposure of membranes to natural waters [31] might also be present in the bare carbon films used in CDLE, although systematic studies on this issue have not been performed yet.

In the current context, a very promising technique will come from combining CDP and CDLE methods. Recall that while CDLE needs a power supply to store ions in activated carbon electrodes, CDP works efficiently with ion selective membranes. Membranes in CDP play the role of the external voltage source in CDLE, generating by themselves a voltage difference between the electrodes. The core of the present approach is the spontaneous generation of charge on the electrodes without the use of either membranes or a power supply. It is just the physicochemical modification of the

carbon particles that produces the required charge.

As previously shown by Ahualli et al. [32], we can attribute the term *soft electrodes* to conductive electrodes made of an activated carbon core and a polyelectrolyte layer, either cationic or anionic. Hence the *soft electrode* (SE) method would allow the generation of electrical energy due to changes in both the EDL capacitance of the carbon electrodes and the Donnan potential of the polyelectrolyte layer when solutions are exchanged. It has been shown that such modification leads to an important reduction of the leakage current [29,30]. Similarly to an auto-generated cycle [26], characteristic of the CDP method, there is no need for an external power supply, and electricity generation is directly produced by the mixing process. Like in the CDLE method, the potential difference in the cell is associated to the processes occurring on the particles themselves without the need of membranes. Hence a relatively thin polyelectrolyte layer suffices and likely results in a decrease of the overall cost of the method.

Although the possibilities of the SE technique as an efficient way of producing clean electrical energy from mixing solutions were demonstrated in a previous work [32], its results have never been compared to those achieved with CDP. However, such a comparison is of a great interest, as both methods share the mechanism of specific charging of each electrode by means of a film on the active carbon layer, and each of them might have its advantages and drawbacks. In addition, it was not explored before whether the characteristics (adsorbed amount, molecular weight, type of polyelectrolyte) of the charged polymer coating in SE might make some difference in the performance of the method. Hence, the purpose of this paper is to compare CDP and SE methods in order to find out whether the mentioned advantages of not needing membranes can be a chance to take the best of both capmix techniques but approaching CDP extracted power. With this aim, we will first analyze the differences between both methods related to potential rise in open circuit voltage (OCV) measurements, and extracted power, that is, the essential information of the capmix cycles. We will also analyze the working principles of soft electrodes for parameter optimization. This will be a first insight into polyelectrolyte layer behavior and is key for the improvement of the SE method.

2. Materials and methods

We used the same laboratory scale cell for SE and CDP experiments [26]. It consists of two parallel graphite collectors coated with carbon films (Voltea B.V., The Netherlands) and facing each other. These two electrodes of 2 × 2 cm² were separated 200 μm. Concentrated (30 g L⁻¹ NaCl) and dilute (1 g L⁻¹ NaCl) saline solutions were alternately fed into the cell at a constant flow rate of 100 mL min⁻¹. Before the start of each experiment, the carbon electrodes were soaked in salt water.

Two ion exchange membranes from Fumatech (Germany) were used for CDP experiments: a Fumasep FAS anion exchange and a Fumasep FKS cation exchange, both of 30–40 μm thickness. For the SE method, soft conductive electrodes were prepared by contacting Voltea carbon films with respectively anionic and cationic polyelectrolyte solutions under magnetic stirring during 12 h. After that time, the electrodes were placed on the cell as shown in Fig. 1. Two anionic polyelectrolytes were tested: poly (sodium 4-styrenesulfonate) or PSS, and poly (acrylic acid) or PAA. The cationic polymers investigated were PDADMAC (poly(diallyldimethyl ammonium chloride)) and PEI (poly(ethyleneimine)). All of them were purchased from Sigma Aldrich (USA) and the typical molecular weights (M_w) selected were: 70 000 and 200 000 g mol⁻¹ for PSS; 100 000–200 000 and 200 000–350 000 g mol⁻¹ for PDADMAC; 15 000 g mol⁻¹ for PAA and 2000 g mol⁻¹ for PEI.

Download English Version:

<https://daneshyari.com/en/article/7730219>

Download Persian Version:

<https://daneshyari.com/article/7730219>

[Daneshyari.com](https://daneshyari.com)