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Analysis and simulation of a blue energy cycle☆

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ABSTRACT

The mixing process of fresh water and seawater releases a significant amount of energy and is a potential source of renewable energy. The so called 'blue energy' or salinity-gradient energy can be harvested by a device consisting of carbon electrodes immersed in an electrolyte solution, based on the principle of capacitive double layer expansion (CDLE). In this study, we have investigated the feasibility of energy production based on the CDLE principle. Experiments and computer simulations were used to study the process. Mesoporous carbon materials, synthesized at the Oak Ridge National Laboratory, were used as electrode materials in the experiments. Neutron imaging of the blue energy cycle was conducted with cylindrical mesoporous carbon electrodes and 0.5 M lithium chloride as the electrolyte solution. For experiments conducted at 0.6 V and 0.9 V applied potential, a voltage increase of 0.061 V and 0.054 V was observed, respectively. From sequences of neutron images obtained for each step of the blue energy cycle, information on the direction and magnitude of lithium ion transport was obtained. A computer code was developed to simulate the process. Experimental data and computer simulations allowed us to predict energy production.

1. Introduction

The energy obtained by salinity-gradients (blue energy) is a promising renewable energy source for the future. In delta areas, where rivers with low-salinity water flow into seawater, the potential for energy recovery is significant. Mixing a high-concentration saline solution with fresh water to produce a brackish solution dissipates more than 2.2 MJ of free energy per m^3 of fresh water treated [1]. This value is equivalent to the potential energy released by the fall of the same volume of water over 220-m height. It has been estimated that the combined power from all large estuaries in the world could provide 2 TW, approximately 20% of today's worldwide energy demand or close to present-day electricity use [2,3]. Since Pattle's pioneering studies in 1954 [1], several technologies have been proposed, including pressure-retarded osmosis [4–7] based on semipermeable membranes and reverse electrodialysis [8–11] based on ion selective membranes, to transform the lost free energy into mechanical or electrical work. However, large scale applications are hindered by high membrane cost and short life due to fouling [12]. Recently, a new method using high-capacitance activated-carbon electrodes based on the contraction/expansion of electrochemical double layers inside pores of macro/mesoporous carbon has been proposed [12–14]. Brogioli [12] proposed the method and conducted an experimental demonstration of the process. The author concluded that the method could produce an acceptable amount of energy. Following on this work, reversible cycles that alternate charging/discharging super-capacitors using saline and fresh water streams have been developed [3,12–18]. These new methods can lead to recovery efficiencies up to 74% of the free energy change [16].

The charging-discharging process inside the pores of the solid electrodes is strongly influenced by the pore size distribution.

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Macroporous materials behave like standard plate capacitors while mesoporous materials behave like cylindrical capacitors. In the case of microporous materials, a 'wire in a cylinder' model seems to describe experimental data [19–21].

The presence of multivalent ions complicates the picture as ionic competition becomes important. In this case effects of charge and ion size play a key role. Recently, processes for ionic separation based on these technologies have been developed [22,23]. Successful segregation by charge has been achieved.

Neutron imaging is a useful technique that can be used to visualize the spatial distribution of certain elements in materials. Neutrons passing through a material can be captured by neutron-absorbing elements, and the resulting spatial neutron distribution can be instantaneously visualized using neutron sensitive scintillators and imaging devices [24–27]. Neutron imaging techniques have been applied to investigate transport of ions in porous carbon electrodes [24–26], as well as quantify the amount of water in fuel cells [27–29] and soil [30,31]. In situ measurements using neutron imaging can be used to elucidate the behavior of ions during blue energy generation.

The goal of this work is to study the recovery efficiency of free energy change by using a neutron imaging technique and a developed theoretical model that simulates ionic transport in mesoporous carbon electrodes. In the present work, neutron imaging experiments were conducted to visualize the ion transport across mesoporous carbon electrodes during the various stages of the capacitive blue energy cycle. The theoretical model allowed transient assessment of the different steps and study of non-uniform phenomena inside the electrodes.

2. Background

Brogioli [12] proposed the new capacitive method based on electric double-layer capacitor theory. The author's experimental set-up consisted of an electrochemical cell made of two porous electrodes submerged into a water saline solution (Fig. 1(a)). Two saline solutions were alternatively used, seawater and fresh water solutions. An external power source allows application of a potential to the arrangement. The external circuit is completed by a resistance (load) and an open/close switch. The author carried out the following cycle: the porous electrodes are first charged at constant potential while the porous electrodes cell is filled with seawater. Then, the circuit is open to 'freeze' the stored charge and the seawater is replaced by a fresh water solution. A third step involves closing the circuit and discharging the stored charge. Finally, the circuit is open again and the fresh water is replaced by seawater. The third step will produce an increase in potential above the original set potential; therefore, allowing surplus electrical work to be performed. The increase in the double layer size produced by decreasing the concentration from seawater (about 0.5 M) to fresh water (about 0.01 M) was thought to be the cause for the potential increase.

Brogioli et al. [13] developed a simple prototype cell of much larger dimensions in order to facilitate testing and further scaling-up of this technology. The authors reported that the amount of energy generated per cycle per unit electrode mass was 20 times greater than the one obtained previously [12]. Brogioli et al. [13] used the Gouy-Chapman-Stern model for electrical double layer (EDL) formation to estimate the energy produced. The authors developed charge density vs. potential curves for different electrolyte concentrations. Then, these curves were used to compare theoretical predictions with experimental results.

Theoretical models can be useful tools to optimize the process. Biesheuvel and Bazant [32] modeled a porous medium made of mostly homogeneous pores using a 1-D transport model. The porous electrode was divided into pore space filled with quasi-neutral electrolyte and a solid matrix. The solution inside the pore space exchanged ions with a charged, thin double-layer "skin" on the electrode matrix. The system was modeled using a porous electrode of length L_{elec} and a thin mass transfer layer just outside the electrode of length L_{SDL}, [32]. The authors' approach is based on Newman's macroscopic porous electrode theory [33], and the same assumptions were made. The porous electrode was thus treated as a homogeneous mixture of charged double layers and quasi-neutral solution. Due to the central part that this model plays in this work a detailed description is included below.

Biesheuvel et al. [34] also presented a porous electrode theory focused on electrodes composed of solid particles that are porous themselves. The pore distribution consists of the interparticle or macroporosity outside the particles through which the ions are transported (transport pathways), and the intra-particle or micropores inside the particles, where electrostatic double layers (EDLs) are formed. The authors used a novel modified-Donnan (mD) approach for the micropores valid for strongly overlapped double layers. This work was based on a previous article by Biesheuvel et al. [35], who studied membrane capacitive deionization. This technology is used for water desalination and consists of placing two ion-exchange membranes in front of two porous electrodes such as that ions are removed from the saline water and stored in the electrodes. The ion-exchange membranes allow for counter-ion transfer from the electrodes into the flow channel while keeping the co-ions inside the electrode structure [35]. The authors described the EDL structure by proposing a modified Donnan model to account for ion transfer into micropores smaller than the Debye length. Similar idea was presented by Revil and Linde [36]. The authors did not determine the charge-potential relationship by solving the Poisson-Boltzmann equation, instead they used a Donnan distribution obtained by equating the chemical potentials of the water molecules and ions between a reservoir of ions and the pore space of the medium.

Rica et al. [15] used Biesheuvel model [33] to analyze the dynamics of extraction of energy from salinity gradients using carbon porous electrodes. The authors studied the time-evolution of the cell voltage observed in experiments. Rica et al. [15] explained the asymmetry on the duration of the solution-change steps performed in open circuit based upon the nonlinear voltage–concentration relationship of the electric double layers and current that redistributes the counter-ions along the depth of the electrode leading to non-uniform charge and salt adsorption. One very appealing characteristic of Biesheuvel et al. models [32,34,35] is that they allow transient analysis of the process steps and also reveal details of the distribution of properties inside the electrode. However, caution should be used in using 1-D models in quantitatively analyzing experimental processes due to the several simplifying assumptions used [15]. Several authors reported excellent agreement between simulation results and experimental data [13,15,32,34].

These articles greatly advanced the state of the theory in this subject. However, in this work we chose to use a transport model similar to the one presented by Biesheuvel et al. [32] due to the fact that the mesoporous carbon electrodes developed at Oak Ridge National Laboratory (ORNL) [37–39] present an almost unimodal pore distribution. The same reason led us to use a model of overlapping EDLs in slit mesopores [40].

3. Materials and methods

3.1. Capacitive energy extraction experiments

A schematic view of the experimental setup for capacitive energy extraction is shown in Fig. 1 (b). The different steps of the