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

42 the blue energy cycle, information on the direction and magnitude of lithium ion transport was
43 obtained. A computer code was developed to simulate the process. Experimental data and
44 computer simulations allowed us to predict energy production.

45 Keywords: Blue Energy, Neutron Imaging, Salinity-gradient Energy

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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 m³ 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 freshwater 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. 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 (Figure 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 sea water 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.

Figure 1. (a) Steps of the blue energy cycle based on the CAPMIX technique. The cell is filled with salt water in the beginning. The steps of the cycle are: charging (Step I), flow of fresh water (Step II), discharging (Step III), and flow of saline water (Step IV). (b) Schematic view of the capacity energy extraction experimental setup. (c) Typical voltage-charge cycle.

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 Figure 1 (b). The different steps of the energy extraction cycle involve opening and closing the circuit to apply electrical potential to the electrodes. The circuit was closed during Steps I and III while it was opened during Steps II and IV. These steps have different feed solutions: seawater of approximately 6,000 ppm was employed during Step I and IV while deionized water was used for Step II and III. Switching the circuit and feed solutions, respectively, can yield compression and expansion of EDLs in the electrodes. A constant flow rate of 46 ml min^{-1} was used during the energy extraction cycle.

3.2 Neutron Imaging Experiments

3.2.1 Material synthesis and characterization

Cylindrical mesoporous carbon electrodes synthesized at the Oak Ridge National Laboratory (ORNL) were used for in-situ measurements of capacitive energy extraction using neutron imaging. The synthesis procedure shown in our previous work [24] was employed to produce monolithic mesoporous carbon electrodes with high porosity. Platinum wires were inserted into the carbon electrodes to allow application of an electrical potential.

Synthesized mesoporous carbon electrodes were characterized using Micromeritics Tristar 3000 that can provide the BET surface area and BJH (Barrett-Joyner-Halenda) pore size distribution. Nitrogen gas was used as the adsorbate for the porosity and surface area characterization of the electrodes.

3.2.2 Flow-through cell for neutron imaging

A special flow-through cylindrical cell was prepared for neutron imaging experiments of capacitive energy extraction. Two cylindrical mesoporous carbon electrodes were placed in the

cell, separated from each other by a glass holder located at the base of one of the electrodes. The flow-through cell was connected to a reservoir where saline solution was stored. The solution was supplied to the flow-through cell via a micropump. The cell was filled up with 70 mL of lithium-6 chloride ($^6\text{LiCl}$) solution of 0.5 M concentration, and the experiments were conducted in a batch mode. Application of electrical potential to the electrodes was performed by connecting the platinum wires, embedded in the carbon electrodes, to a power supply (HP 3632A; Hewlett Packard, CO). After Step I, the salt solution was drained out and the cell was filled with pure deuterium oxide (D_2O). After Step III, D_2O was again drained out from the solution and replaced by $^6\text{LiCl}$ solution. Lithium-6 isotope was used as it has a high neutron attenuation coefficient of 940.97 barns. D_2O instead of H_2O was used because hydrogen absorbs neutrons and can inhibit the ability to visualize lithium ions in both the electrodes and the bulk solution.

3.2.3 Neutron imaging principle

Interaction of a neutron beam with a material decreases the neutron intensity because of absorption of neutrons by the constituent elements. The loss of neutrons results in attenuation of the neutron beam. The attenuated beam is captured by a detector, which transforms neutrons into visible light. A charge coupled device camera takes images using the visible light, which can show the spatial distribution of neutron-absorbing elements inside the material.

The attenuation of the neutron beam can be expressed using the Beer–Lambert equation:

$$I = I_0 e^{-\mu\delta} \quad (1)$$

where I is the beam intensity at the sample thickness δ , I_0 is the incident beam intensity, and μ is the attenuation coefficient which can be determined via experiments or theory. The Beer-Lambert equation indicates that if μ is a constant value, the neutron intensity can

exponentially decrease as a function of δ . Effects of the constituent elements of a material can be taken into account through μ [24]. Further details of neutron imaging are available elsewhere [24-26].

3.2.4 Neutron imaging experiments

Neutron imaging experiments were performed at the CG-1D neutron beam line at the ORNL High Flux Isotope Reactor. A schematic of the neutron imaging experimental arrangement is illustrated in the TOC Graphic. Lithium chloride ($^6\text{LiCl}$) solution was supplied to the cell for neutron imaging experiments during the various steps of the capacitive energy extraction. $^6\text{LiCl}$ was selected since it is a 1-1 symmetric electrolyte like NaCl [26]. The experiments were conducted in four typical steps for capacitive energy extraction:

Step I (Charging): The cell was filled up with $^6\text{LiCl}$ solution of 0.5 M. The electrodes were charged through application of external potential. The circuit was closed and there was current flow through the circuit.

Step II (Switching feed to fresh water): The circuit was opened and the cell was filled up with D_2O solution. The potential across the electrodes was measured as a function of time.

Step III (Discharging): The circuit was closed and the current flow was in reverse direction.

Step IV (Switching feed to saltwater): The circuit was opened and the cell was filled up with $^6\text{LiCl}$ solution again. This step closed the cycle for each experiment.

During all four steps of the cycle, the potential across the electrodes was measured continuously as a function of time. Neutron images obtained during the experiments were analyzed using iMARS, a neutron sciences software developed at ORNL [41, 42].

3.3 Theoretical Model

A modification of the model originally proposed by Biesheuvel and Bazant [32] with volume average equations derived by Gabitto and Tsouris [43] (also see Sharma et al. [26, 44]) was used for simulating the charging and discharging steps. Details of the model are presented below. The simulation of the switching steps was done using a developed diffusion-in-porous-media model coupled with a potential estimation scheme described below. This process allowed us to obtain profiles of all the variables calculated in the process as a function of position inside the electrode and time. In order to study the behavior of operating parameters, we calculated average values of potential, concentration, charge, etc., over the electrode thickness. The energy produced by the process is obtained by plotting the evolution of potential vs. charge during a cycle and calculating the area of the enclosed space.

3.3.1 Model for charging and discharging steps

The 1-D transport model in porous media used in this work is very similar to the one proposed by Biesheuvel and Bazant [32]. The porous electrode was divided into a 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. More details can be found in the original work by Biesheuvel and Bazant [32]. The volume averaged transport equations inside the porous electrodes can be written in dimensionless form as (Gabbitto and Tsouris, [43]):

$$\partial c^*/\partial t^* = D_{eff} \nabla^2 c^* - \varepsilon J_{salt}^* \quad (2)$$

255 where c^* is the dimensionless ion concentration in the pore space at position x (C/C_∞), with C_∞
 256 the bulk salt concentration, J_{salt}^* is the dimensionless salt adsorption term, D_{eff} is the effective
 257 diffusivity, t^* is a dimensionless time obtained by rescaling the dimensional time τ_d with $\tau_d =$
 258 L_{elec}^2 / D_0 , $\varepsilon = \lambda_D / h_p$, λ_D is the characteristic Debye length, and the pore thickness h_p is defined
 259 as the ratio of the electrode porosity to the electrode specific surface area, $h_p = \varepsilon_\alpha / a_v$.

260 In dimensionless form, the charge conservation equation becomes:

$$261 \quad \nabla \cdot (c^* \nabla \phi) = \varepsilon J_{\text{charge}}^* \quad (3)$$

262 Here, ϕ is the potential made dimensionless by dividing by the thermal voltage (V_T) given by
 263 $R T / F$, where R is the universal gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute
 264 temperature, F is the Faraday constant (the number of coulombs per mole of electrons: $F =$
 265 $9.648 \times 10^4 \text{ C mol}^{-1}$), and J_{charge}^* is dimensionless rate of charge removal from the liquid phase.

266 In the stagnant diffusion layer (SDL), equations similar to (2) and (3) are used:

$$267 \quad \partial c^* / \partial t^* = \nabla^2 c^* \quad (4)$$

$$268 \quad \text{and } \nabla \cdot (c^* \nabla \phi) = 0. \quad (5)$$

269 In order to close the porous electrode model, the dimensionless rate of charge removal from
 270 the liquid phase, J_{charge}^* , was related to the dimensionless charge density, $-q^*$, by:

$$271 \quad \partial q^* / \partial t^* = J_{\text{charge}}^*, \quad (6)$$

272 and the dimensionless salt adsorption term J_{salt}^* to w^* by:

$$273 \quad \partial w^* / \partial t^* = J_{\text{salt}}^* \quad (7)$$

274 J_{salt}^* and J_{charge}^* were made dimensionless by multiplication by $L_{\text{elec}} / J_{\text{lim}} / \lambda_D$, where $J_{\text{lim}} =$
 275 $2D_0VC_\infty/L_{\text{elec}}$, and D_0 is the free solution diffusivity .

276 The relationship between the dimensionless potential in the solution filling the pore space (ϕ)
 277 and the solid phase potential (ϕ_1) was calculated using the approach proposed by Yang et al. [40]
 278 for the case of strong EDL overlapping. In the case of small slit-type pore, the EDL is confined
 279 by two charged flat surfaces; therefore, the EDLs of the two flat surfaces begin to overlap in the
 280 central region, as the slit width decreases.

281 The relationship between the dimensionless potential in the solution filling the pore space (ϕ)
 282 and the equivalent solid-phase potential (ϕ_1) can be calculated by a combination of a charge-free
 283 Stern layer of constant capacity and potential difference $\Delta\phi_S$ and a diffuse layer with potential
 284 difference $\Delta\phi_D$ (Biesheuvel and Bazant [32]).

$$285 \quad \phi_1 - \phi = \Delta\phi_S + \Delta\phi_D \quad (8)$$

286 The voltage drop through the Stern layer is related to the dimensionless charge density, q^* , by:

$$287 \quad q^* = -\Delta\phi_S/\delta \quad (9)$$

288 where $\delta = \lambda_S/\lambda_D$ and λ_S is the effective thickness of the Stern layer. The dimensionless charge
 289 density in the diffuse layer is calculated by Yang et al. [40]:

$$290 \quad q^* = -[2 c^* (\cosh(\phi_D/V_T) - \cosh(\phi_M/V_T))]^{0.5} \quad (10)$$

291 where q^* is the excess charge in the diffuse layer divided by $2 \lambda_D C_\infty$; c^* is the dimensionless
 292 ion concentration in the pore space at position x (C/C_∞), ϕ_D is the potential at the outer
 293 Helmholtz plane, and ϕ_M is the potential at the pore middle point. The dimensionless excess salt
 294 adsorption (w^*) is calculated from,

$$295 \quad w^* = \int_D^\infty (c^* - c_\infty^*) dx \quad (11)$$

The dimensionless concentration is calculated as a function of position by first calculating the potential as a function of position and, then, using the Poisson-Boltzmann equation to compute the concentration profile inside the pore. Finally, equation (11) is numerically solved.

The dimensionless potential profile is calculated using the following model developed in our previous work [26]. The distance $2L$ can be defined as the distance between the outer Helmholtz' planes of the two flat surfaces. The potential profile can be obtained as a function of distance using an analytical expression [26]:

$$\phi = 2 \ln \left\{ \frac{1 - K e^{-x}}{1 + K e^{-x}} \right\} \quad (12)$$

$$\text{with } x = \frac{X}{\lambda_D} \text{ and } K = -\tanh\left(\frac{\phi_D}{4}\right),$$

where X is the dimensional distance and ϕ_D is the potential at the outer Helmholtz plane.

Equation 12 can also be used to obtain the potential profile for the opposing flat surface after replacing x with y :

$$y = \frac{2L}{\lambda_D} - x \quad (13)$$

Using the principle of superposition and eqs 12 and 13, the inner potential profile of the slit pore can be obtained as:

$$\phi = A_1 \phi(x) + A_2 \phi(y) \quad (14)$$

where A_1 and A_2 are constants determined to fit the boundary conditions at the flat surfaces, $x = 0$, and $x = 2L/\lambda_D$. It can be shown that:

$$A_1 = A_2 = \frac{\phi_D}{2} / \ln \left[\frac{(1 - K)(1 - K e^{-2L/\lambda_D})}{(1 + K)(1 + K e^{-2L/\lambda_D})} \right] \quad (15)$$

The electrolyte potential profile inside the slit pore can be determined by solving for A_1 and A_2 and introducing the values into equation 14.

The discharging step is modeled by using the same routine. In this case, at a predetermined time, we set the potential in the solid matrix to the minimum value and run the model again.

3.3.2 Model for switching steps

There are no mass source terms, and the amount of charge remains constant; therefore, the mass transport equation inside the porous electrodes can be written in dimensionless form as,

$$\partial c^*/\partial t^* = D_{\text{eff}} \nabla^2 c^* \quad (16)$$

For a given surface charge density q^* , the potential ϕ_D in the OHP is given by equation (9), which can be rearranged as:

$$\phi_D = \phi_I - q^* \delta \quad (17)$$

The value of q^* is the last value computed during the previous charging/discharging step, assuming it remains constant during the switching step. For an ideal 1:1 monovalent salt solution, the potential ϕ_M in the middle of the pore is given by:

$$\phi_M = V_T \text{acosh}\left\{\cosh\left(\phi_D / V_T\right) - \frac{q^{*2}}{2c}\right\} \quad (18)$$

The potential over the EDL at equilibrium, over the whole cell, assuming symmetrical behavior of the two electrodes, is calculated by:

$$V_{\text{cell}} = 2 (\phi_I - \phi_M) \quad (19)$$

Eqs. (17) to (19) give mathematical justification to the process proposed in this work. A combination of these equations shows that, as the salt concentration decreases, λ_D increases and the cell voltage, V_{cell} , also increases [13].

4. Results and Discussion

4.1 Characterization of Synthesized Carbon Electrodes

Figure 2 shows nitrogen adsorption isotherms and the BJH pore size distribution of the synthesized carbon electrodes. It was found that the mesoporous-carbon electrodes have a specific surface area of $365 \text{ m}^2 \text{ g}^{-1}$. The average pore size and the pore volume at $P/P_0 = 0.995$ were 10 nm and $0.43 \text{ cm}^3 \text{ g}^{-1}$, respectively.

4.2 Capacitive Energy Extraction

The experiments were based on sequentially flowing fresh and saline water through the cell. The voltage across the electrodes, current, and conductivity of the solution were continuously monitored throughout the entire duration of the experiment. Experiments were conducted to determine the voltage variation across the electrodes during the switching Step II (when deionized water is flushed through the cell) and switching Step IV (when a saltwater feed is introduced).

Results from experiments conducted at 0.6 V are shown in Figure 3 (a). The cell potential increased up to 0.662 V from a starting value of 0.616 V within 5 hours for Step II. The long duration of the experiment is due to the thickness of the carbon electrodes used in the experiments. These results provide experimental confirmation that it is possible to recover the mixing energy using a capacitive method. Figure 3 (a) shows that the potential increasing rate was not constant with time. The cell potential increased very fast at short times, but it slowed down at longer times. In the case of Step IV, after the potential dropped due to discharging, we can see that the cell potential decreased from a starting value of approximately 0.61 V down to 0.596 V in a 5 hours period. Similar results, not shown here, were found for experiments conducted at 0.9 V.

360
 361 **Figure 2.** (i) Nitrogen adsorption isotherms and (ii) BJH pore-size distributions for the mesoporous
 362 carbon used in neutron imaging experiments. The pore surface area of the mesoporous carbon is 365
 363 m^2/g , and the average pore size is around 10 nm.

Figure 3. (a) Time variation of measured cell voltage for Step II and Step IV for the blue-energy cycle at applied 0.616 V. (b) Change in electrical potential of the electrodes during Step II of the capacitive energy extraction cycle.

4.3 Neutron Imaging Results for Capacitive Energy Extraction

In-situ measurements using the neutron imaging technique have been performed to investigate transport of ions within the electrodes and in bulk solution during capacitive energy extraction. Figure 4 shows time-series images of Step I obtained under applied potential $V = 0.3, 0.6$, and 0.9 V. Here, the images were normalized using the first image of each operational condition and iMARs [42]. The brightness of the images represents ${}^6\text{Li}^+$ concentration; the more the lithium ions are, the darker the image is. Application of the electric potential resulted in electrostatic interactions among ${}^6\text{Li}^+$, Cl^- , and charged electrodes; here, chloride ions are assumed to be invisible because their absorption cross section is significantly smaller than that of lithium ions [26, 45]. For all cases, many lithium ions were adsorbed on the right electrode, which was negatively biased, while the left electrode was positively biased. For $V = 0.6$ and 0.9 V, ${}^6\text{Li}^+$ ions desorbed from the left electrode due to electrostatic repulsion, suggesting that Cl^- ions diffuse inside this electrode because of electrostatic attraction. The effect of electrostatic attraction between ${}^6\text{Li}^+$ and Cl^- ions can be observed in neutron images obtained with 0.3 V applied potential. Compared to the other two cases, the electrodes in this case were submerged in the ${}^6\text{LiCl}$ solution of 0.5 M for a much longer period of time (approximately 12 h) before starting the experiment, leading to uptake of ions in the absence of applied potential. When a 0.3 -V potential was applied, excess chloride ions initially adsorbed onto the left electrode attracted ${}^6\text{Li}^+$ for charge neutralization, until equilibrium was reached. A similar ion-ion interaction phenomenon was observed during desalination experiments of low- and high-salinity solutions using a capacitive deionization process [24, 26]. It is also observed in Figure 4 that, at 0.9 V, the ${}^6\text{Li}^+$ ion concentration in the right electrode is more uniformly distributed than at lower voltages, probably because of a faster ion diffusion rate due to a stronger driving force. After Step I, both

Figure 4. Neutron images for Step I of the capacitive energy extraction cycle. The images were normalized using the first neutron image at time 0. As time progresses, the right (negative) electrode becomes darker because it attracts ${}^6\text{Li}^+$ ions. The left (positive electrode) should adsorb mostly Cl^- ions; however, at the lowest potential of 0.3 V, it also adsorbs ${}^6\text{Li}^+$ ions, as the images reveal. This phenomenon is due to the interaction between ${}^6\text{Li}^+$ and Cl^- ions. At 0.9 V, the distribution of ${}^6\text{Li}^+$ ions on the right electrode is more uniform than at lower voltages, probably because of a faster transport rate due to a stronger driving force.

electrodes contained ${}^6\text{Li}^+$ (Figure 5), suggesting that invisible Cl^- ions are also present inside the pores of both electrode. The neutron imaging results suggest that, at the end of Step 1, the negative (right) electrode accumulated mostly ${}^6\text{Li}^+$ ions and the positive (left) electrode accumulated mostly Cl^- ions; however, a smaller fraction of co-ions also adsorbs onto the electrodes due to ion-ion interactions between ${}^6\text{Li}^+$ and Cl^- ions.

Figure 6 indicates time-dependent changes in the ${}^6\text{Li}^+$ ion distribution in the cell during Step II. In this step, the ionic strength of the bulk solution was much lower than that in Step I, and no external potential was applied. These differences between Steps I and II led to the release of many ions from the electrodes into the bulk solution. This is evident from the series of images, as

Figure 5. Neutron images after Step I of the capacitive energy extraction cycle. The images were taken after the solution was removed and normalized using the clean-electrode neutron images. As expected, a higher potential between the two electrodes leads to a lighter positive electrode (with more chloride ions and less lithium ions) and a darker negative electrode (with more lithium ions and less chloride ions).

Figure 6. Neutron images for Step II of the capacitive energy extraction cycle. The images were normalized using the first neutron image at time 0. As time progresses, both the right (negative) electrode and the left (positive electrode) become lighter revealing that $^6\text{Li}^+$ ions (and probably Cl^- ions) desorb from both electrodes when the bulk ion concentration decreases sharply. As the electrodes become lighter, the bulk solution becomes darker due to release of neutron-absorbing $^6\text{Li}^+$ ions from the electrodes to the surrounding solution.

the region inside the electrodes (particularly near the edges) becomes lighter and the bulk solution becomes darker with increasing time. During this step, the potential across the electrodes increased continuously, as a function of time. For example, the 2-h operation of Step II, after applying 0.3 V in Step I, yielded an electrical potential of 0.33 V (Figure 3b). An increase in the electrical potential during Step II was also observed for the cases of 0.6-V and 0.9-V applied potential (not shown).

The behavior of ions observed during Step III was similar to that during a typical capacitive deionization processes (not shown). In Step III, the circuit was closed and the electrodes were discharged to the initial potential. As the potential decreased, adsorption/desorption of ${}^6\text{Li}^+$ and Cl^- ions occurred on the electrodes to counterbalance the electrode charge. ${}^6\text{Li}^+$ and Cl^- ions were released from the electrodes because of the lower potential, thereby increasing the ion concentration of the bulk solution.

Neutron images of Step IV for an applied potential of 0.6 V are shown in Figure 7. In this step, the circuit was opened and the cell was again filled up with the ${}^6\text{LiCl}$ solution. Both electrodes became darker as lithium ions, as well as chloride ions, diffused inside the electrodes. As a result, the ${}^6\text{Li}^+$ concentration of the bulk solution decreased. The images of Figure 7 reveal that ${}^6\text{Li}^+$ ions migrated inside both the electrodes in Step IV, and a similar behavior is assumed for the invisible Cl^- ions. This behavior is not ideal because, returning to Step I of the cycle, a fraction of the energy provided will be wasted in driving co-ions from the electrodes to the bulk solution. An ideal behavior, in terms of energy recovery, would be to have only counterion adsorption by the electrodes. Such behavior can be achieved by coating the electrodes with ion-specific membranes.

Figure 7. Neutron images for Step IV of the capacitive energy extraction cycle with $V = 0.6$ V. The images were normalized using the first neutron image at time 0. As time progresses, both the right (negative) electrode and the left (positive electrode) become darker revealing that ${}^6\text{Li}^+$ ions (and probably Cl^- ions) adsorb on both electrodes when the bulk ion concentration increases. As the electrodes become darker, the bulk solution becomes lighter due to uptake of neutron-absorbing ${}^6\text{Li}^+$ ions by the electrodes.

4.4 Simulation Results

The theoretical model was implemented by developing a computer code that solves numerically the full set of four differential equations plus four algebraic equations using a global iteration loop. More details about the code are given by Sharma et al. [26, 44]. Typical results calculated using the blue energy model are shown in Figures 8. The computer code calculates point values inside the porous electrode and the SDL. However, in order to study the behavior of operating parameters we present calculated average values of all the operating variables over the electrode thickness.

Figure 8(a) shows the variation of the average salt concentration in a complete cycle. Step I shows the electrode charging behavior. At short times, the average concentration decreases very

fast (supercapacitor regime) while, at longer times, the salt concentration increases slowly due to diffusion from the bulk of the solution (desalination regime). Step II shows the behavior due to switching the feed to a fresh water solution. The average concentration decreases continuously as the low concentration solution replaces the initial high concentration solution. This process is driven by diffusion, therefore, it is slow. Step III depicts the discharging behavior. At short times, the concentration increases sharply due to fast release of ions into the pores, but at longer times, the concentration decreases due to diffusion into the solution outside the electrode. Step IV shows the behavior during the switching to a saltwater feed. There is a continuous increase in pore concentration due to replacement of the fresh water solution by a higher-concentration electrolyte.

Figure 8(b) shows typical results for the predicted cell voltage variation during a cycle. It shows a very fast increase during the charging process. In the critical Step II the model predicts a potential increase above the applied voltage due to the EDL thickness increase produced by the continuous decrease in salt concentration. These results provide the theoretical justification for the energy production by capacitive mixing. The results also show a very fast decrease during the discharge period. During Step IV the cell potential decreases due to the EDL thickness decrease caused by the increasing salt concentration inside the pores produced by the replacement of the fresh water solution by saltwater.

A typical blue energy cycle is shown in Figure 8(c). The area inside the enclosed curve gives the amount of energy produced by the cycle. In Figure 8(c), the charge (Q) is negative because the behavior of a positive electrode is depicted.

Comparisons between experimental data and simulation results are shown in Figures 9 and 10. The experimental data shown in Figure 3(a) have been expressed as dimensionless quantities. A

matching between experimental data and simulation results has been achieved by using the electrode effective area as an adjustable parameter in the model. This procedure is similar to the one described by Sharma et al. [44]; however, in this work we did not use other parameters as was the case previously. We also introduced a modification in the computer code that allowed us to increase the range of effective area values used.

It can be seen in Figure 9 that the theoretical model predicts a linear increase of cell voltage with time. The experimental data show a more complex picture. At short times, the experimental cell voltage increases faster than the predicted result. However, at longer times the experimental time variation decreases until falling below the predicted results. The experimental potential increase with respect to the starting potential is 7.5% compared to 11% for the predicted value.

A comparison of the experimental and predicted cycle is shown in Figure 10. The solid lines enclose the simulated cycle, while the broken lines enclose the experimental cycle. These results show that the measured cycle produced 50% of the predicted energy value. This is because the maximum experimental potential value in Step II is below the predicted one and the minimum experimental value is above the predicted one. These findings are in agreement with the information presented in Figure 9. The agreement between simulation results and experimental data could be considered very good taking into account that no fitting of our simulation results to the experimental data has been done. Direct comparison of our results with published ones is not possible due to differences in electrode properties and the fact that some authors [46] have used a variable Stern layer capacitance as an adjustable parameter in their simulations. In this work, we have kept the capacitance of the Stern layer constant and equal to 0.32 F/m^2 . A comparison, not shown here, with the data reported by Rica et al. [47] showed very good qualitative agreement. Same qualitative agreement has also been observed with other authors [15, 46]. Consideration of

the results presented in Figures 9 and 10 shows that, in order to increase energy recovery, it is not only necessary to increase the cell potential in Step II, but also to decrease the cell potential in Step IV. A possible way to achieve this is to decrease further the salt concentration inside the porous electrode during Step II and increase further the salt concentration during Step IV. This behavior can be achieved by increasing the operation time for steps II and IV. However, the efficiency of the global process should be considered; i.e., use of more cycles per unit time with lower efficiency per cycle compared to fewer cycles per unit time with higher cycle efficiency.

Figure 8. Changes in the salt concentration, potential, and charge in a typical blue energy cycle: (a) average pore salt concentration variation with time during a complete cycle; (b) dimensionless potential variation with time during a complete cycle; (c) potential-charge density variation during a complete cycle. The internal area determines the energy generated.

Figure 9. Comparison of measured and simulated cell voltages.

Figure 10. Comparison of simulated and experimentally estimated energy produced.

5. Conclusions

In the present study, we used experimental and theoretical tools to study capacitive mixing as a way to recover free energy of mixing (blue energy). Modified capacitive deionization and neutron imaging experiments of the blue energy cycle were carried out to observe the direction of ion transport across the electrodes during the various stages of the cycle. In the deionization and neutron imaging experiments with cycles carried out from 0.3 V to 0.9 V applied voltage, we observed an increase in voltage during Step II when low-salinity water replaced high-salinity solution in the cell. Thus, it can be deduced that a voltage range of 0.3-0.9 V is suitable for the operation of blue energy cycle. Neutron imaging was employed to visualize the transient behavior of ions during the different steps of the blue energy cycle.

A theoretical model of the blue energy cycle was also presented. It uses a homogeneous-porous-media model to simulate the charging and discharging steps, and it is based on a diffusion model coupled with a potential estimation scheme to simulate the switching steps.

Experimental data and simulation results show that it is possible to increase the potential above the applied cell potential, producing energy. The measured energy recovery was found to be smaller than the predicted one. Experimental and theoretical tools produce in depth knowledge on the ion transport mechanisms during the different steps of the blue-energy cycle and, therefore, can help in devising strategies on how to maximize the energy produced per cycle.

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733 TOC Graphic

Neutron imaging experimental arrangement for blue energy experiments

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