Characterization of Ion Transport and -Sorption in a Carbon Based Porous Electrode for Desalination Purposes

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New and more efficient water desalination technologies have been a topic of incipient research over the past few decades. Although the focus has been placed on the improvement of membrane-based desalination methods such as reverse osmosis, the development of new high surface area carbon-based-electrode materials have brought substantial interest towards capacitive deionization (CDI), a novel technique that uses an electric field to separate the ionic species from the water. Part of the new interest on CDI is its ability to store and return a fraction of the energy used in the desalination process. This characteristic is not common to other electric-field-based desalination methods such as electrodeionization and electrodialysis reversal where none of the input energy is recoverable. This paper presents work conducted to analyze the energy recovery, thermodynamic efficiency, and ionic adsorption/desorption rates in a CDI cell using different salt concentration solutions and various flow rates. Voltage and electrical current measurements are conducted during the desalination and electrode regeneration processes and used to evaluate the energy recovery ratio. Salinity measurements of the inflow and outflow stream concentrations using conductivity probes, alongside the current measurements, are used to calculate ion adsorption efficiency. Two analytical species transport models are developed to estimate the net ionic adsorption rates in a steady-state and nonsaturated porous electrode scenario. Finally, the convective and electrokinetic transport times are compared and their effect on desalination performance is presented. Steady test results for outlet to inlet concentration ratio show a strong dependence on flow rate and concentration independence for dilute solutions. In addition, transient test results indicate that the net electrical energy requirement is dependent on the number of carbon electrode regeneration cycles, which is thought to be due to imperfect regeneration. The energy requirements and adsorption/desorption rate analyses conducted for this water-desalination process could be extended to other ion-adsorption applications such as the reprocessing of lubricants or spent nuclear fuels in a near future.
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1 Introduction

With the current population of the planet soaring to approximately 7×10^9 [1], there has never been a more appropriate time to consider the state of the world's natural resources. In particular, clean water resources have become more strained as the population increases [2,3]; in fact, the continents with the largest populations, Asia and Africa, have some of the fewest drinking water resources per person [4]. Attention has consequently been focused on converting abundant seawater resources into potable water through various methods [3,5–7].

The existing desalination processes may be grouped according to the method used to separate the dissolved ions: membrane-based, thermal, electrical, or a combination of any of the previous. In membrane-based desalination, water is purified using various membranes and include methods such as reverse osmosis (RO) and membrane electrodialysis [3,8,9]. Thermal methods utilize a phase change to separate the dissolved ions from the fluid and include multistage flash distillation (MSF), multieffect distillation (MED), and mechanical vapor compression [3]. Electrical desalination involves using an electric potential to cause the electromigration of ions out of the solution. Examples include electrodialysis and capacitive deionization (CDI) [3,5,6]. Of all these methods, reverse osmosis and multistage flash distillation are currently the most popular. However, comparison of these methods in Table 1 indicates that the specific energy requirement of CDI is the least compared to these popular methods, underscoring its potential as a practical future desalination method.

Capacitive deionization is a novel desalination technique where an electric field is applied to separate ions from a solution stream and capture them onto high surface area electrodes [3,6]. Since the electrodes have finite surface area, this electrical desalination method consists of two subprocesses shown in the schematics of Fig. 1: desalination, where ions are adsorbed onto the electrodes; and regeneration, where ions are desorbed from the electrodes. The uniqueness of CDI as a desalination method relies on the capability to store the ions, so that they can be used during regeneration to partly recover the desalination energy input.

During the desalination process, the electric potential provided by a power supply generates an electric field across the electrodes to extract ions from the solution to the corresponding electrode depending on their polarities. Therefore, the resulting output solution has a lower ionic concentration. The net movement of charged particles creates an electric current that decreases as the porous electrodes are saturated. When the capacity of the storage medium is reached and no more ions can be collected, there would

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Table 1 Comparison of the specific energy required by CDI and other popular water desalination methods for equal desalination ratios [2,8]

Technology	Energy required (kW·h·m^{-3})
RO	2.9 – 3.7
MSF	4
MED	5
CDI	1.1–2.0

be no variation between the ionic concentration of the inlet and outlet solution until the system is regenerated.

Although regeneration of the CDI system could be performed by short-circuiting the electrodes [10], some authors suggest the inversion of their polarity and use of selective membranes to speed up this process [5]. Regeneration by short-circuiting the electrodes creates an electric current through the discharge of stored ions resulting in a recovery of part of the energy stored during ion adsorption. Because of its capability to partially recover the input energy, a CDI system would require a significantly lower energy input (about 2 kWh·m^{-3} for a 70% concentration reduction) [3].

Although the concept of capacitive deionization dates back to the late 1960s and early 1970s, it was not until the development of new high surface porous materials in the 1990s that capacitive deionization became an attractive technology [3,5,6]. The use of electrodes made of high surface area conductive materials increases the system capacitance to adsorb and retain electric charge [11,12]. Therefore, evaluating and measuring the adsorption capability of various materials such as carbon aerogel and carbon nanotubes plays an important role in evaluating the performance of a CDI system. Various authors [3,11,13] have suggested determining the electrode's capacitance using electrochemical analysis techniques and assuming that both the

Fig. 1 (*a*) Overview of desalination cycle. Voltage difference applied across the electrodes induce opposite electrode charges to attract and adsorb the ions. (*b*) Overview of regeneration cycle. Ion concentration on the electrode surfaces decrease together with the electrode charge, due to current flow across the resistor.

desalination and regeneration processes are nonfaradic. On the other hand, Zhao et al. [14] determined the effective surface area and electrode capacitance from measurement of the equilibrium salt adsorption and electrode charge. Furthermore, various authors have used the charge efficiency (ratio of the amount of salt adsorbed to the charge on the electrode) of the desalination process as a whole to evaluate the adsorption of ions [14], but have not looked at how it varies with time within each desalination process.

A critical aspect in assessing the feasibility of the CDI process is evaluating how efficiently the system can purify an input solution for continuous operation with consecutive desalination and regeneration cycles. The present paper pursues four specific objectives: (1) Firstly, experimental evaluation of the variations in the energetic performance of a CDI system when the desalination and regeneration processes are alternated as in experiments conducted by Anderson et al. [3], and Welgemoed and Schutte [5]. (2) Secondly, experimental evaluation of the influence of solution flow rate on the maximum desalination percentage attained in a CDI system using dilute solutions. (3) Thirdly, introducing the evaluation of the time variation in outlet solution concentration and using adsorption efficiency as tools to optimize the operation of an alternating desalination-regeneration process in a CDI system. (4) Lastly, presenting two simplified analytical models for the maximum desalination percentage expected and their validation with experimental data.

2 Methodology

2.1 Experimental Setup. Desalination experiments were conducted at the Multiscale Thermal-Fluids Laboratory at The University of Texas at Austin. The setup for a typical test includes a Harvard Apparatus PHD 2000 syringe pump to pump the solution at a constant flow rate ranging from 0.5 cm^3·min^{-1} to 100 cm^3·min^{-1}; an eDAQ Flow-Thru Conductivity Electrode ET908 and a Vernier conductivity probe to measure the conductivity of the solution at the exit of the cell; an Agilent E3647A power supply; an Omega® FLR-1601A flow meter; an Omega® PX429-10WDDU5V differential pressure transducer to evaluate the pressure drop along the CDI cell; a 30.1 Ω electric resistor to short-circuit the CDI cell during its regeneration; and a custom fabricated CDI cell. Figure 2 shows the actual experimental setup and a schematic.

A schematic of the CDI cell is shown in Fig. 3. The cell contains two metal electrodes made of titanium foil, two high surface area carbon aerogel sheets from Marketech Technologies with a nominal surface area of 600 m^2·g^{-1} and dimensions of 2.5 × 25 cm, and a polymer mesh divider of 2 mm thickness.

2.2 Experimental Procedure. During the experiments, a salt water solution contained in multiple syringes was pumped through the cell by the Harvard Apparatus PHD 2000 pump and monitored by the Omega FLR-1601A flow meter. Before starting a desalination process, the conductivity readings were checked to be constant to assure that variations in outlet conductivity were due to the adsorption of ions within the cell and not due to the irregularities of the inlet solution conductivity. Then, a constant potential difference of 1 V was applied between the two electrodes using the Agilent E3647A power supply to cause the desalination of the solution stream. As ions were adsorbed onto the carbon aerogels, their concentration in the solution, and thus the conductivity of the solution, decreased. This change was measured by the eDAQ Flow-Thru Conductivity Electrode ET908 and was used to calculate the adsorption rate of the ions. The current supplied to the system was also recorded using the National Instruments USB 6008 DAQ, which along with the known constant voltage could be used to obtain the energy input of the desalination process.

To start the regeneration of the system, the two electrodes were connected by an electric resistor and the voltage drop across this
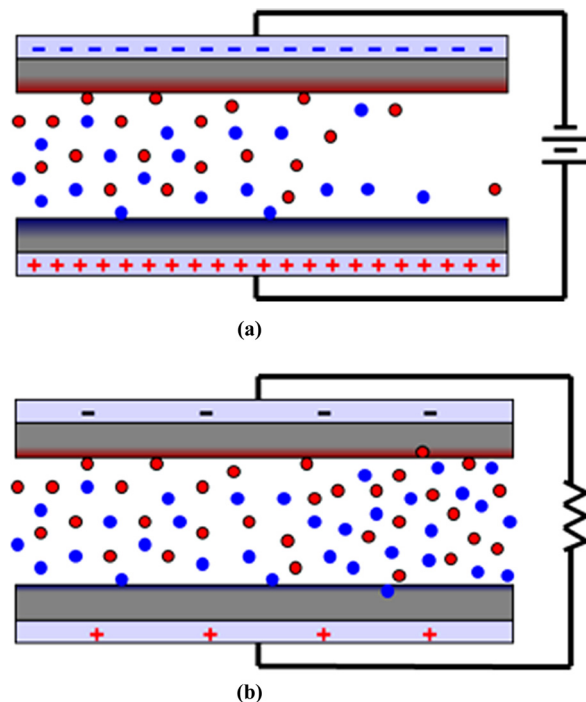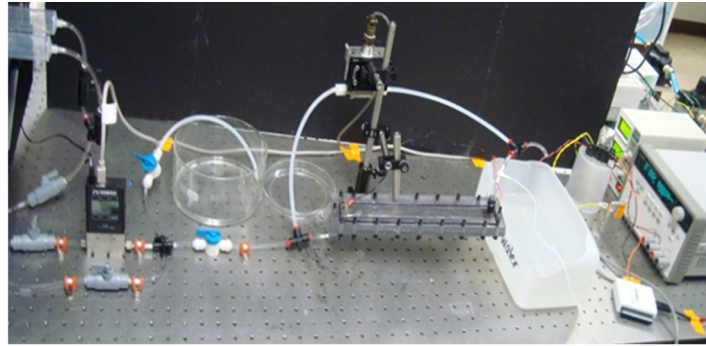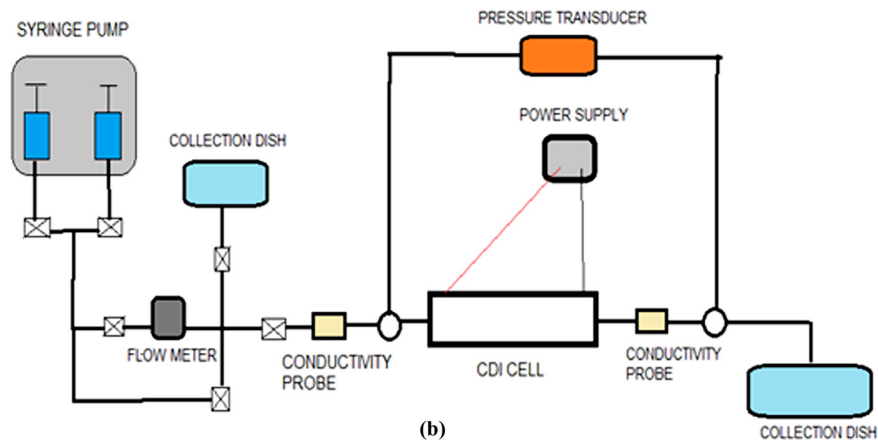
Fig. 2 (*a*) **Actual experimental setup, and** (*b*) **schematic of the experimental setup**
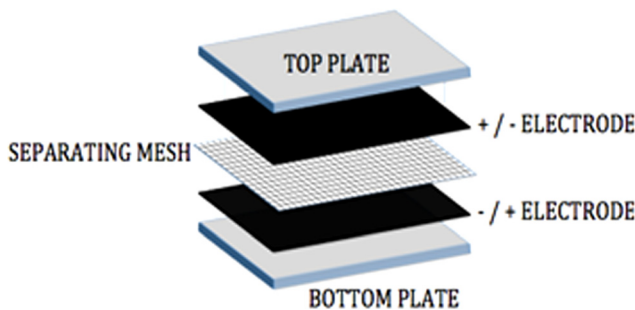

Fig. 3   Schematic of CDI cell

known resistance was measured by the USB 6008 DAQ to calculate the recovered energy. The increase in the conductivity due to the ion release from the aerogels was again measured by the eDAQ Flow-Thru Conductivity Electrode ET908 to calculate the desorption rate of ions.

2.3   Transient and Steady Tests. Two types of tests were conducted to characterize the capacitive deionization system: steady and transient. The main difference between the steady and transient tests is the duration of the desalination and regeneration processes.

During a steady test, desalination occurred until the carbon aerogels were completely saturated and the system reached a steady state. This saturation point is noted when the conductivity of the outlet returns to the inlet conductivity value, meaning that there is no net ion adsorption within the cell. Once the desalination was complete, the regeneration process was started and continued until the solution conductivity decreased back to the inlet conductivity level. Like desalination, this leads to no net ion desorption and indicates that the system has reached a steady state.

During a transient test, the transition from desalination to regeneration was not made at the saturation point; but instead was conducted when the salinity of the outlet solution reached a minimum. Regeneration continued until the salinity reached a maximum and consecutive desalination and regeneration cycles were performed based on the local maxima and minima of the conductivity.

Figures 4(*a*) and 4(*b*) show examples of conductivity and current data from a transient test. It may be seen that the outlet conductivity, and thus concentration, shows an oscillatory behavior, increasing during regeneration and decreasing during desalination. The circuit current exhibits a decaying behavior, peaking at the initial desalination/regeneration and then decreasing as the driving potential decreases in time.

2.4   Energy and Efficiency Analysis. To evaluate the performance of the CDI system at different flow rates, initial concentration, and test type situations, two metrics were calculated: energy recovery ratio and adsorption efficiency.

2.4.1   Energy Recovery. The energy recovery ratio is the ratio of energy generated during regeneration to the energy consumed during desalination, calculated using Eqs. (1) and (2)

$$E_{\mathrm{desal}} = \int V_{\mathrm{desal}} \cdot I(t) \cdot dt \qquad (1)$$

$$E_{\mathrm{regen}} = \int \frac{V_{\mathrm{regen}}^2(t)}{R} dt \qquad (2)$$

where V_{desal} is the desalination voltage applied to the CDI cell (V), I is the electrical current (A) measured by the power supply during desalination, R is the resistance (Ω) between the electrodes during regeneration and V_{regen} is the voltage drop across the mentioned resistance during the regeneration process.
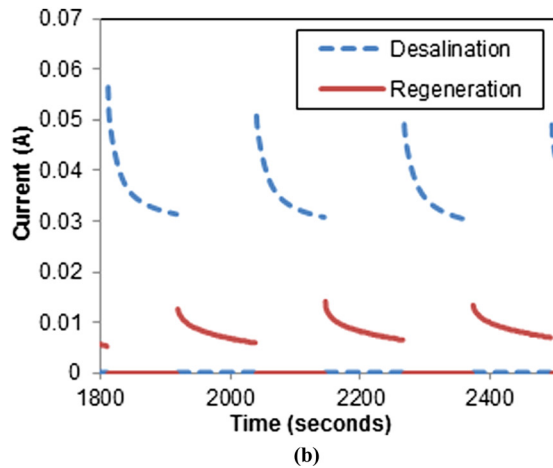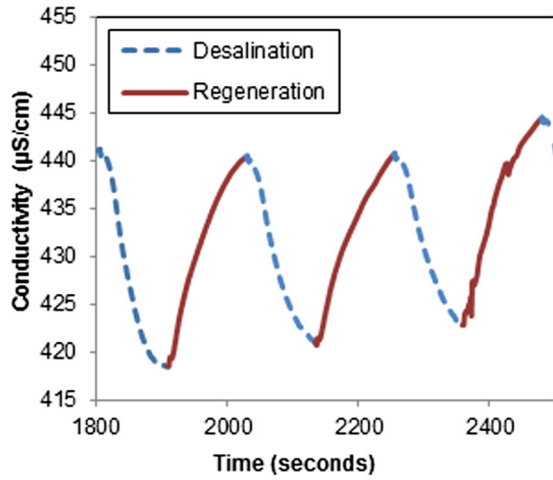
(a)

(b)

Fig. 4 (*a*) **Outlet conductivity as a function of time for a transient test, and** (*b*) **circuit current as a function of time for a transient test**

2.4.2 Adsorption Efficiency. This metric was defined as the ratio of the number of ions adsorbed, N_{ads}, to the number of electrons displaced from one electrode to another, N_{e-}. This efficiency was calculated from the current and conductivity data by using Eqs. (3) and (4)

$$N_{\text{ads}} = \frac{N_A \cdot Q \cdot \int (\sigma_{\text{in}} - \sigma_{\text{out}}) dt}{F \cdot \left(v^{cl^-} + v^{Na^+} \right)} \tag{3}$$

$$N_{e-} = \frac{\int I(t) \cdot dt}{e} \tag{4}$$

Here, N_A is the Avogadro's number (mol^{-1}), Q is the solution flow rate, σ_{in} and σ_{out} are the inlet and outlet solution conductivities ($\text{S} \cdot \text{m}^{-1}$), respectively, F is the Faraday's constant ($\text{C} \cdot \text{mol}^{-1}$), and v^{cl^-} and v^{Na^+} are the chloride and sodium ion mobilities ($\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$), respectively, e is the elementary charge.

2.5 Simplified Analytical Models for Steady State Tests. Analysis of data from the steady test results led research in the direction of two simplified analytical mass transfer models to find a relationship between the flow rate and the ratio of minimum and initial conductivities. By assuming a steady adsorption process and infinite adsorption capacity of porous carbon aerogel (which is an acceptable approximation for dilute solutions) the CDI cell was analyzed as a one dimensional conservation of spe-
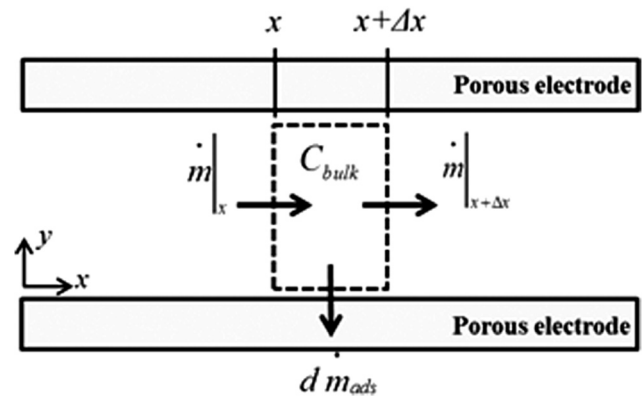
Fig. 5   Control volume analysis for salt adsorption

cies problem illustrated in Fig. 5. Two models can be developed for a CDI system based on two different boundary conditions: constant electrode surface concentration and constant adsorption rate (analogous to the heat transfer boundary conditions of constant surface temperature and constant heat transfer rate, respectively).

2.5.1 Constant Electrode Concentration. Assuming a steady adsorption process and infinite electrode adsorption capacity, the molar flow rates given in Fig. 5 can be expressed as

$$\dot{m}|_x = C_{\text{bulk}}|_x \cdot Q \tag{5}$$

$$d\dot{m}_{\text{ads}} = C_{\text{bulk}}|_x \cdot V_{ek} \cdot W \cdot \Delta x \tag{6}$$

where x (m) is the distance from the CDI cell inlet, W (m) is the channel width, V_{ek} ($\text{m} \cdot \text{s}^{-1}$) is the electrokinetic velocity at which the ions are adsorbed onto the aerogel and C_{bulk} ($\text{mol} \cdot \text{m}^{-3}$) is the bulk ion concentration of the fluid within the cell and is defined by Eq. (7)

$$C_{\text{bulk}}(x) = \left. \frac{W \cdot \int_0^H C(y) \cdot U(y) \cdot dy}{Q} \right|_x \tag{7}$$

where C is the local ionic concentration ($\text{moles} \cdot \text{m}^{-3}$), H (m) is the distance between porous electrodes (thickness of the polymer spacer). In this model, the adsorption flux was modeled as the product of the bulk concentration and the electrokinetic velocity.

By defining the bulk concentration as in Eq. (7) and expressing the mass flow rates as in Eqs. (5) and (6), one might apply the conservation of species analysis and obtain the 1D governing equation of the system as

$$\frac{dC_{\text{bulk}}(x)}{dx} + \frac{V_{ek} \cdot W \cdot x}{Q} C_{\text{bulk}}(x) = 0 \tag{8}$$

Solving Eq. (8) with the boundary condition $C_{\text{bulk}}(x=0) = C_{\text{in}}$, the concentration along the cell is expected to have an exponential decay behavior and the outlet to inlet concentration ratio is given as Eq. (9)

$$\frac{C_{\text{out}}}{C_{\text{in}}} = e^{\left(\frac{-W \cdot L}{Q} V_{ek} \right)} \tag{9}$$

where C_{out} ($\text{mol} \cdot \text{m}^{-3}$) is the outlet concentration, C_{in} ($\text{mol} \cdot \text{m}^{-3}$) is the inlet concentration and L (m) is the length of the cell from inlet to outlet.

As seen in the derivation of the governing transport equation and in the definition of ionic adsorption term, this model is the

solution to a fully developed flow between parallel plates problem, with bulk concentration driven mass transport into the plates with constant zero concentration. As such, adsorption is directly proportional to the bulk concentration and the resultant concentration behavior along the flow direction is an exponential decay, as expected for such boundary conditions. This type of boundary condition and corresponding model solution is applicable to low flow rate conditions, where the convective time is large compared to the ionic electrodiffusion time. This allows for homogeneous distribution of the ionic concentration throughout the bulk, and hence a bulk concentration dependent adsorption rate.

2.5.2 Constant Adsorption Rate. For this second model, the ion concentration along the cell is expected to be linearly decreasing, which can be described using kinematic arguments. Figure 6 portrays the movement of individual ions flowing through the CDI cell for three different cases. In the first case, the counterion that is furthest away from its respective electrode is adsorbed onto the aerogel before reaching the outlet, which means that the outlet concentration will be read as zero. In the second case, the same ion reaches the aerogel at the very end of the cell, just barely being adsorbed, but one would again expect an output concentration of zero. Therefore, one would try to operate the system closer to the second case than the first one to increase the output while still reaching 100% purity. In the third case, it is impossible for the cell to adsorb all of the ions in the solution. Instead, the conductivity would decrease to a certain portion of the initial value depending on the flow rate and the outlet to inlet concentration ratio, given in Eq. (10), would be proportional to the distance b that is traveled by an ion towards its respective electrode before reaching the outlet, shown in Fig. 6.

$$\frac{C_{out}}{C_{in}} = 1 - \frac{b}{H} \tag{10}$$

Distance b can be obtained from a kinematic analysis of the ions by equating the time it takes to navigate the length of the cell and the time it takes for an ion to travel a distance of b moving at a constant velocity of V_{ek}

$$\frac{L \cdot W \cdot H}{Q} = \frac{b}{V_{ek}} \tag{11}$$

This means that ions closer to their respective electrodes than a distance of b at the inlet are adsorbed and ions further to their electrodes than a distance of b at the inlet are not adsorbed. Therefore, the outlet to inlet concentration ratio for the second model proposed is given as

$$\frac{C_{out}}{C_{in}} = 1 - \frac{V_{ek} \cdot W \cdot L}{Q} \tag{12}$$

This model, which assumes constant electrokinetic velocity throughout the CDI cell and uses simple kinematic arguments for ionic motion, corresponds to a flow between parallel plates problem, with constant adsorption flux at the plate surface. This analogy can be naturally drawn if one considers the paths of same

charge ions inside the CDI cell, which come out to be parallel using the previous assumptions. If the inlet concentration is uniform and the ions move parallel to each other, the surface adsorption should be constant. This is seen as a linear decrease in bulk concentration, as expected for a constant surface flux (or adsorption rate) model. This type of boundary condition and corresponding model solution is applicable to high flow rate conditions, where the convective time is small compared to the ionic electrodiffusion time. This prevents redistribution of the ions throughout the bulk of the solution, and hence a constant adsorption rate based on the entrance concentration.

Equations (9) and (12) are the outcome of the analytical models corresponding to a constant electrode concentration and a constant adsorption rate boundary condition, respectively. These two models are compared with experimental data and further discussed in Sec. 3.4.

3 Results and Discussion

3.1 Energy Recovery—Transient Tests. The energy recovery ratio of the system was monitored throughout the transient tests, since it is a unique and important property of capacitive deionization. Even with a simple lab-scale experimental setup, energy recovery ratios above 10% were achievable, which is a promising result for the CDI system.

When the energy recovery performances of the CDI system at different flow rates are compared, the energy recovery ratio is observed to increase with the number of cycles performed, independent of the flow rate. This behavior is illustrated in Fig. 7 for three transient tests at different flow rates, using an aqueous solution containing $0.2 \, \text{mg} \cdot \text{cm}^{-3}$ of NaCl. The energy recovery associated with this solution at three different flow rates are shown in Fig. 7.

The results show an increase in energy recovery with respect to cycle number, in accordance with the experiments performed using an electrochemical parametric pumping system by Oren [6]. In this study, it is postulated that with each additional cycle, the amount of ions adsorbed that remain at the electrode surface increases because the CDI cell cannot be fully regenerated. This incremental increase in the amount of nonexpelled ions might augment the energy recovery during later cycles because of a combination of two important factors. First, with each additional cycle, fewer ions can be adsorbed before saturating the electrode, resulting in less power input. Second, during regeneration, a larger number of Na^+ and Cl^- ions are rinsed resulting in larger amounts of energy recovery due to a more saturated electrode and the repulsion forces between ions of the same polarity.

This increment of the remaining ions from previous cycles in each electrode would also decrease their respective ionic adsorption capacity, which would cause faster saturation of the electrodes. This, in turn, would lead to a decrease in the amount of ions extracted from the solution in the subsequent cycle; thus lowering
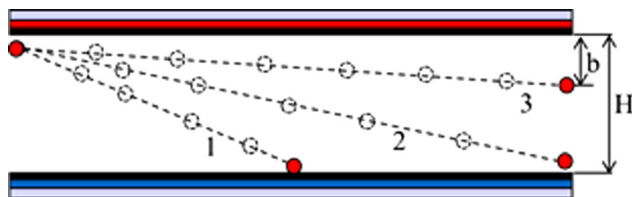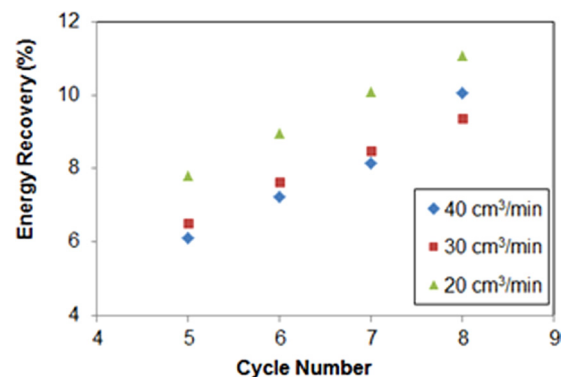

Fig. 6 Ion movement in CDI cell. The paths 1, 2 and 3 correspond to the ionic paths when the convective time is larger, equal, and smaller than the electrokinetic time, respectively.

Fig. 7 Energy recovery based on cycle number

Table 2 Input/recovered energies and amounts of adsorption during cycles 5 to 8 of a transient CDI experiment with a concentration of 0.2 mg·cm^{-3} and flow rate of 40 cm^3·min^{-1}

Cycle	Energy in (J)	Energy out (J)	Ions adsorbed (mg)
5	3.79	0.23	2.33
6	3.67	0.27	2.28
7	3.59	0.29	2.21
8	3.46	0.33	2.16

the adsorption capability of the system, as seen in Table 2. This decrease in system performance due to remnant ions is the main motivation for reversing electrode polarity during regeneration, to clean the electrodes more efficiently.

Table 2 shows the input and recovered energies for cycles 5 to 8 of the transient test at 40 cm^3·min^{-1}. This table also shows that the input energy decreases with cycle number, while the recovered energy increases. As explained before, this behavior is expected from a CDI cell which is not fully regenerated at each cycle and it causes the amount of ions adsorbed at each desalination cycle to decrease.

3.2 Maximum Desalination Percentage in Steady Tests. The longer duration steady tests are used to analyze the adsorption process at different flow rate and concentration conditions. These tests provide a temporal overview of desalination process until complete carbon aerogel saturation, including conductivity and current data, from which the extent of concentration decrease, total number of adsorbed ions, energy input/recovery and adsorption efficiency can be calculated.

The first important finding obtained from these tests was that the minimum outlet to inlet concentration ratio (maximum desalination percentage) that can be obtained at a constant flow rate does not vary with solution concentration, provided that the solution is dilute. This finding is illustrated in Fig. 8, where the minimum dimensionless conductivities are approximately the same for three different solution concentrations.

The second important finding was that the minimum outlet to inlet concentration ratio that can be obtained at a constant inlet concentration is highly dependent on solution flow rate through the cell. This is exemplified in Fig. 9, where three tests at different flow rates are shown. It can be seen that flow rate and minimum outlet concentration are directly proportional, which is in parallel with the model predictions presented in Sec. 2.5.

The main reason for this concentration independence and flow rate dependence of the outlet to inlet concentration ratio is that when using dilute solutions, the electrode saturation effects are negligible and the fraction of ions adsorbed is only a function of their residence time within the cell.
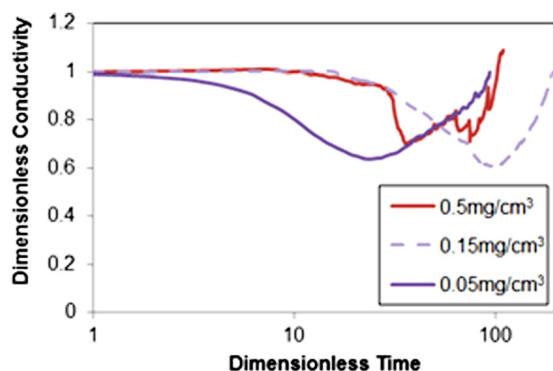

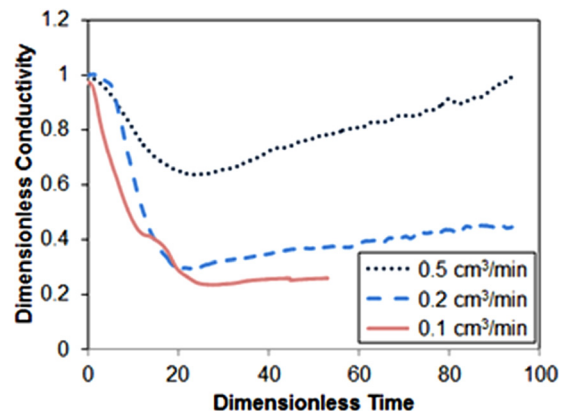**Fig. 9 Steady tests at varying flow rates at a constant solution concentration of 0.05 mg·cm^{-3}**

3.3 Optimization of a CDI System Operation: Adsorption Efficiency. The time behavior of adsorption efficiency for a sample steady test, together with the outlet concentration, can be seen in Fig. 10. At the beginning of the desalination process, the outlet conductivity decreases rapidly, until it reaches its minimum and stays constant until saturation effects become significant. After 10 hs of desalination, saturation effects start to become dominant and the adsorption rate decreases, resulting in an increase in outlet conductivity until it reaches the inlet conductivity and the aerogels are completely saturated. During this sample desalination process, the adsorption efficiency increases rapidly up to its maximum value, stays roughly constant between hours 3–14 and then decreases as the saturation effects increase. By using such an approach, one can find the optimum adsorption efficiency point for a specific flow rate and implement that time as the desalination time for transient operation of a CDI system.

It should be noted that the adsorption efficiency values are only around 1% due to the very dilute solution used for that specific sample test. The plateau of conductivity and adsorption efficiency seen in this test may also not be present for different flow rates and solution concentrations. Therefore, one should perform a steady test at the exact operating conditions to be able to optimize the transient operation of a CDI system, as demonstrated in Ref. [15], or rely on a detailed CDI system model, similar to those found in Refs. [14,16], to obtain the transient outlet conductivity behavior and input current data numerically, needed to establish the transient operating points.

3.4 Analytical Models. Steady tests at various flow rates and at salt concentrations of 0.025 and 0.05 mg·cm^{-3} were conducted to validate the models presented in this paper. The results are

Fig. 8 Steady tests at varying solution concentrations at a constant flow rate of 0.5 cm^3·min^{-1}
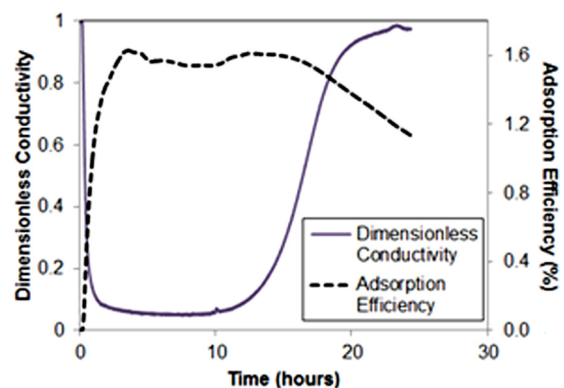

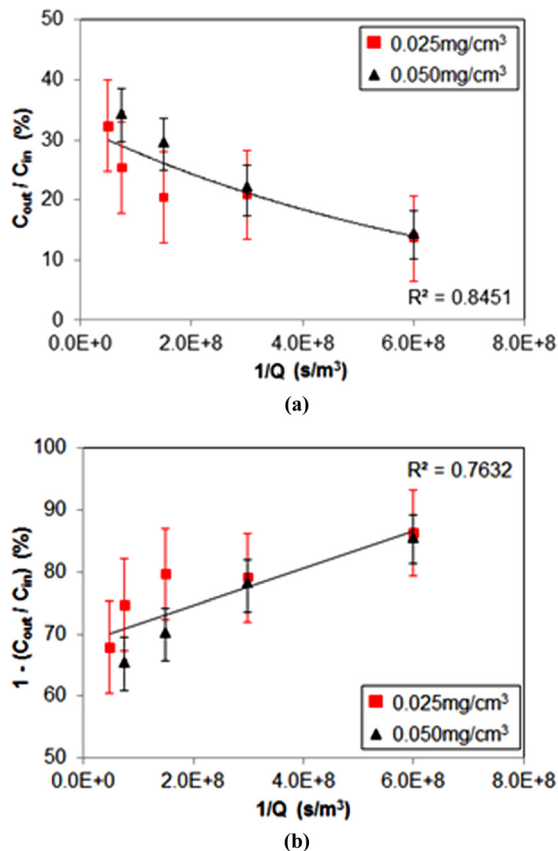**Fig. 10 Characteristic conductivity and adsorption efficiency for steady tests**

Fig. 11 (*a*) Constant aerogel concentration model results for constant concentration steady tests, and (*b*) constant aerogel adsorption model results for constant concentration steady tests

shown in Figs. 11(*a*) and 11(*b*) for the constant aerogel concentration and the constant aerogel adsorption rate assumptions, respectively.

Two different curve fits were applied onto the experimental data according to the models proposed in Sec. 2.5: an exponential one for constant aerogel concentration and a linear one for constant aerogel adsorption rate. The values for V_{ek} were then approximated from the coefficients of $1/Q$ as 2×10^{-7} and 5.1×10^{-6} (m·s^{-1}) for the constant concentration and constant adsorption rate models, respectively. It can be seen that both models provide a rough approximation of the minimum outlet to inlet concentration ratio, but the constant aerogel concentration assumption provides a better correlation with the experimental data. Further improvements on this approach, together with a model for electrode saturation is presented in [17].

4 Conclusions

In this study, two types of experiments were performed on a laboratory scale capacitive deionization cell: Steady tests, performed to understand the ionic adsorption process and transient tests, performed to analyze the energetics of the CDI cell.

Experimental data from steady tests suggest that the minimum outlet to inlet concentration ratio obtained by the CDI cell is directly proportional to the flow rate and is independent of the solution concentration provided that the solution is dilute. This implies that as long as saturation of the porous electrodes is not a dominant factor, the outlet purity of a flow through CDI system is related to the incidence time of the solution inside the cell. However, it was seen that both the energy efficiency and adsorption efficiency are dependent on the inlet solution concentration.

Two analytical models have been presented to study, as a first approximation, the adsorption rate of ions in solutions of very low ionic concentration. It was seen that the constant aerogel surface concentration model correlates better with the experimental data for the flow rates used during the tests. However, more experiments can be conducted, as in Ref. [17], to see if these two models are suitable for different flow rates. It is not expected for these models to be accurate at brackish water concentration levels for this lab-scale experimental setup; therefore future tests are going to be performed at systematically increasing solution concentrations to inspect the region of validity of current models and to come up with new models to include saturation effects.

Analysis of the adsorption efficiency during a steady desalination process suggests the existence of a region where the adsorption efficiency, defined as the ratio of ions adsorbed to the number of electrons displaced, is at a maximum. Further analysis of this peak of adsorption efficiency would allow for more efficient operation of CDI systems in transient mode. Such an approach is demonstrated in Ref. [15].

The energy input and energy recovery results from the transient tests indicate that the CDI cell cannot be regenerated completely, leaving remnant ions on the porous electrodes, which decreases the number of ions adsorbed and the energy input for the next desalination cycle and increase the energy recovery for the next regeneration cycle. This is observed as an increase in energy recovery ratio as the cycle number increases, but it also means a decrease in ionic adsorption performance. Therefore, one should not use energy recovery by itself as a measure of energy efficiency of a CDI system and further research is going to be pursued in evaluation of transient energetics.

References

[1] U.S. Census Bureau, 2012, "U.S. & World Population Clocks," May 15, 2012, http://www.census.gov/main/www/popclock.html
[2] Chenoweth, J., 2008, "Minimum Water Requirement for Social and Economic Development," Desalination, **229**(1–3), pp. 245–256.
[3] Anderson, M. A., Cudero, A. L., and Palma, J., 2010, "Capacitive Deionization as an Electrochemical Means of Saving Energy and Delivering Clean Water. Comparison to Present Desalination Practices: Will It Compete?" Electrochim. Acta, **55**(12), pp. 3845–3856.
[4] Food and Agriculture Organization of the United Nations, 2010, "Freshwater Availability-Precipitation and Internal Renewable Water Resources (IRWR)," September 2012, http://www.fao.org/nr/aquastat
[5] Welgemoed, T. J., and Schutte, C. F., 2005, "Capacitive Deionization Technology^{TM}: An Alternative Desalination Solution," Desalination, **183**(1–3), pp. 327–340.
[6] Oren, Y., 2008, "Capacitive Deionization (CDI) for Desalination and Water Treatment—Past, Present and Future (A Review)," Desalination, **228**(1–3), pp. 10–29.
[7] Kamal, I., 2008, "Myth and Reality of the Hybrid Desalination Process," Desalination, **230**(1–3), pp. 269–280.
[8] Vial, D., and Doussau, G., 2003, "The Use of Microfiltration Membranes for Seawater Pre-Treatment Prior to Reverse Osmosis Membranes," Desalination, **153**(1–3), pp. 141–147.
[9] Voros, N. G., Maroulis, Z. B., and Marinos-Kouris, D., 1996, "Salt and Water Permeability in Reverse Osmosis Membranes," Desalination, **104**(3), pp. 141–154.
[10] Dermentzis, K., and Ouzounis, K., 2008, "Continuous Capacitive Deionization-Electrodialysis Reversal Through Electrostatic Shielding for Desalination and Deionization of Water," Electrochim. Acta, **53**(24), pp. 7123–7130.
[11] Lim, J.-A., Park, N.-S., Park, J.-S., and Choi, J.-H., 2009, "Fabrication and Characterization of a Porous Carbon Electrode for Desalination of Brackish Water," Desalination, **238**(1–3), pp. 37–42.
[12] Zhai, Y., Dou, Y., Zhao, D., Fulvio, P. F., Mayes, R. T., and Dai, S., 2011, "Carbon Materials for Chemical Capacitive Energy Storage," Adv. Mater., **23**(42), pp. 4828–4850.

[13] Park, K.-K., Lee, J.-B., Park, P.-Y., Yoon, S.-W., Moon, J.-S., Eum, H.-M., and Lee, C.-W., 2007, "Development of a Carbon Sheet Electrode for Electrosorption Desalination," Desalination, **206**(1–3), pp. 86–91.

[14] Zhao, R., Biesheuvel, P. M., Miedema, H., Bruning, H., and van der Wal, A., 2009, "Charge Efficiency: A Functional Tool to Probe the Double-Layer Structure Inside of Porous Electrodes and Application in the Modeling of Capacitive Deionization," J. Phys. Chem. Lett., **1**(1), pp. 205–210.

[15] Demirer, O. N., Naylor, R., Rios Perez, C. A., Wilkes, E., and Hidrovo, C., "Energetic Performance Optimization of a Capacitive Deionization System Operating With Transient Cycles and Brackish Water," Desalination (submitted).

[16] Biesheuvel, P. M., van Limpt, B., and van der Wal, A., 2009, "Dynamic Adsorption/Desorption Process Model for Capacitive Deionization," J. Phys. Chem. C, **113**(14), pp. 5636–5640.

[17] Rios Perez, C. A., Demirer, O. N., Clifton, R. L., Naylor, R. M., and Hidrovo, C. H., 2013, "Macro Analysis of the Electro-Adsorption Process in Low Concentration NaCl Solutions for Water Desalination Applications," J. Electrochem. Soc., **160**(3), pp. E13–E21.