Critical review article

# Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete?

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## ARTICLE INFO

## ABSTRACT

Potable water as well as water for agriculture and industry is critical to human habitation on this planet. We have been squandering and polluting this precious resource and are now in need of finding cost competitive newer technologies for reclaiming this valuable life-sustaining liquid. Capacitive deionization (CDI) is an electrochemical water treatment process that holds the promise of not only being a commercially viable alternative for treating water but for saving energy as well. CDI works by sequestering ions, or other charged species, in the electrical double layer of ultracapacitors. While removing these ions, one actually stores capacitive energy. If one recovers this energy efficiently, this process likely consumes less power than any competing technology. This paper reviews current methods for treating water in comparison to the state of art of the CDI process.

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## Contents

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## 1. Introduction—water and energy

Hall and Day [1] have written a recent and compelling article related to the plethora of environmental problems facing present and future generations of human inhabitants on the face of the Earth. Hall and Day suggest that instead of thinking about "peak oil" we have now arrived at "peak everything". However, they admit that scientists and engineers may be able to avoid immediate calamity through technological solutions to these shortages (this review article on capacitive deionization (CDI) is related to one of these technological solutions). Thus, our near term priorities should be focused on solving global warming, providing a stable and sufficient energy supply, and delivering clean and potable water to the World's people. These later three priorities are directly connected. Global warming is tied to our prodigious demand for energy and the consequent burning of fossil fuels. Furthermore, energy and water are also related. Energy is needed to deliver water and water is needed to generate energy [2,3]. Indeed, one does not site a nuclear power plant in the middle of the desert but rather near a major water body such as a river, lake or the sea. By the same token, we are likely not able to produce energy such as bio-fuels without a sufficient supply of water. On the other hand, we need large quantities of energy to desalinate seawater for potable use. In this review, we first examine the relationships between energy and water particularly with respect to the major methods of desalination focusing finally on capacitive deionization as a potential means of solving the energy–water problems simultaneously.

At the turn of this 21st century, Shawn Tully wrote an article in Fortune magazine indicating that water would be the "oil of this century" [4]. Indeed, major companies marketing drinking water like France's Suez and Vivendi have been betting their future revenues on the scarcity and higher price of water. Fig. 1 shows distributed rainfalls worldwide as well as the per capita availability of water on each continent [5]. It can readily be noticed that the continents having the majority of people, Asia and Africa, also have the least amount of water. Furthermore, as illustrated in Fig. 2, much of the water in developing areas is being used for agriculture leaving very little for human consumption [5].
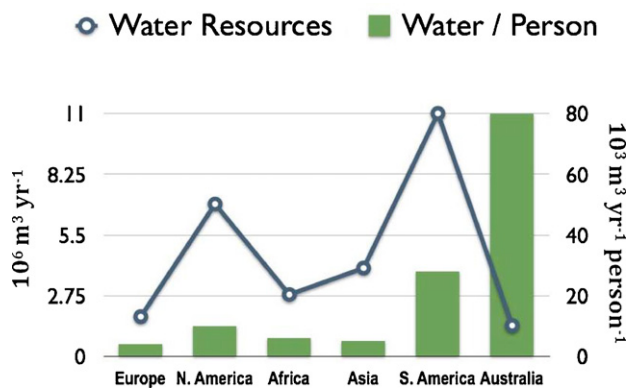
It stands to reason that if most of the 98% of our waters are either sea or brackish waters, we must find newer, more efficient, and cost effective means of removing salts from these waters. Indeed, major cities such as Sydney, Perth, Singapore, Los Angeles, Johannesburg, Jubail, Ras Laffan (Qatar) and Miami are either building or designing huge new desalination plants. We, the authors of this article believe, as some select others, that CDI may ultimately provide a competitive means of delivering potable waters and energy savings at the same time. However, to be competitive, CDI must compare favorably with more established methods both in terms of capital and operational costs.

## 2. Water from the sea—current methods of desalination

Typical concentration of dissolved salts in seawater and brackish water are 35,000 and 1000 mg/L, respectively. The most widely used processes for desalination include membrane separation systems: reverse osmosis (RO), and electrodialysis (ED); and thermal separations including: multistage flash distillation (MSF), multi-effect distillation (MED) and mechanical vapor compression (MVC). Among these processes, RO and MSF methods are employed in the bulk of the plants (90%) to desalinate seawater worldwide [6].

A visual summary of all these processes and their impact on the desalination market is presented in Figs. 3 and 4 adopted from the review of Chaudhry [7]. Among membrane based plants, 86% belong to Revere Osmosis plants while electrodialysis represents only 14%. As also illustrated, while there are more plants using RO membranes than thermal methods, the total amount of water processed by both is almost equal. Electrodialysis has the particularity that, while being a membrane process, the driving force is a potential applied between two electrodes; the same driving force as the CDI process. Thus, we will further analyze the electrodialysis technology below and compare it with CDI [7].

Reverse osmosis is the fastest growing method of desalination but it would not have been possible without the seminal discovery by, Loeb and Sourirajan [8] that transformed membrane separation from a laboratory to an industrial process. The flux of the first Loeb–Sourirajan reverse osmosis membrane was 10 times higher than that of any membrane then available and made reverse osmosis a potentially practical method of desalting water. In this review article, we hope to show that new materials and electrode configurations may also allow for a similar break-through in the CDI process.
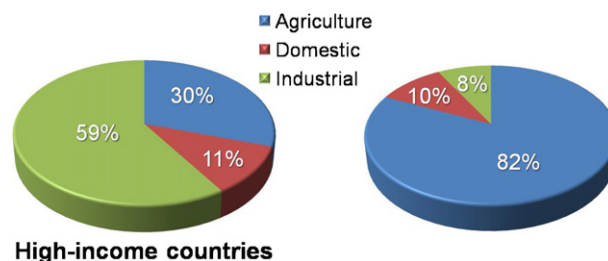


**Fig. 1.** Worldwide water resources per capita and level of rainfall as a function of continent.



**Fig. 2.** The type of water use by sector for developing and high-income countries.
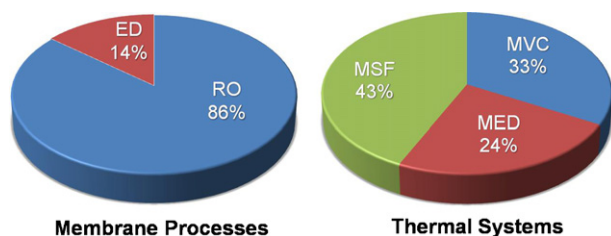
**Fig. 3.** Percentage of membrane and thermal desalination plants worldwide.

## 2.1. Energy required for desalination

RO competes favorably with MSF in regard to energy required: 2.9–3.7 kWh/m$^3$ of water treated for RO vs. 4 kWh/m$^3$ for MSF processes. The latter figure of 4 kWh/m$^3$ of seawater treated is true only if MSF is cited with a working power plant to reduce the heat required to drive this thermal separation process. Furthermore, these values do not consider the recovery of the energy in the pressurized concentrated reject by means such as a Pelton turbine or an isobaric chamber. In this case, it is suggested that energy consumption is reduced to 1 kWh/m$^3$ [7]. However, as Semiat exposes in his recent review [2], a wide variety of energy consumption values are given for desalting processes and some confusion arises when comparisons are tried.

Regardless of the process (RO, MFS, ED or CDI) being used to remove salts from sea or brackish waters, thermodynamically we can calculate the energy required. The minimum energy (work) needed to separate ions from a solution is around 1.1 kWh/m$^3$ for seawater (35,000 ppm) and 0.12 kWh/m$^3$ and for brackish water (4000 ppm) in both cases depending on the recovery [2,9,10]. However, these minimum theoretical values depend upon the input–output flow concentration ratio [9]. For example, if such ratio is 0.5, energy consumption increases to 1.6 and 0.17 kWh/m$^3$, respectively, and if the ratio increases to 0.7, consumption will be 2.0 and 0.21, respectively. Biesheuvel has shown [9] that reversible work needed per unit volume to produce a dilute stream scales with the volume ratio (relationship between inlet and outlet volumes and thus to salt concentration differences), and as a consequence, the minimum work required increases at high water recovery values. In fact, if the concentrated stream becomes infinitely concentrated the required work will be infinite [9].

## 2.2. Capital, operational and maintenance costs for desalination

As stated above, cost of desalination is tied greatly to both, the desalination method and the size of the plant with smaller plants (<1 million gallons per day (MGD), 3790 m$^3$/day) costing over 1.3 dollars/m$^3$ (5 $/kgal) [0.13 cents/L] of seawater treated as opposed to larger plants (>10 MGD) being able to deliver potable water for as low as 0.4 dollars/m$^3$ (1.5 $/kgal) [0.04 cents/L]. In the case of brackish water, the costs vary between 0.10–1 dollars/m$^3$ (0.4–4 $/kgal) [0.01–0.1 cents/L] [7,11]. Borsani and Rebagliati
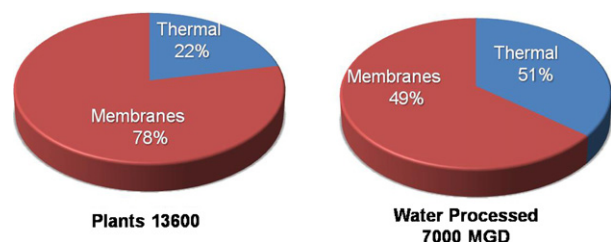


**Fig. 4.** Percentage of membrane and thermal desalination plants worldwide and water processed by these plants. MGD: million gallons per day.

**Table 1**
Types of cost associated with operation and maintenance processes for the major types of desalination plants worldwide.

| Type of cost | MSF (KUS$) | MED (KUS$) | RO (KUS$) |
|---|---|---|---|
| Chemicals for cleaning | 1500 | 1000 | 2500 |
| Operational chemicals | 50 | 100 | 250 |
| People for operations | 400 | 600 | 500 |
| People for maintenance | 100 | 175 | 100 |
| Membranes | NA | NA | 2000 |
| Other | 300 | 200 | 250 |
| Total | 2350 | 2075 | 5600 |

[6] compared the costs associated with operation and maintenance, as well as other costs such as energy, capital cost, etc. for a $170 \times 10^3$ m$^3$/day (45 MGD) [$170 \times 10^6$ L/day] plant delivering potable water located in the Middle East (Gulf Water). Tables 1 and 2 are adopted from their paper. A couple of points can be noted. Energy costs are slightly higher for MSF and MED compared to RO plants. Major operational cost for RO is related to membrane replacement. A recent review analyzing all the information in the literature regarding water desalination cost as a function of the type and size of the plant can be found in Ref. [11].

## 3. Electrodialysis for desalinating brackish waters

### 3.1. Background

Electrodialysis is the closest cousin of capacitive deionization systems and has been successfully used for the desalination of brackish waters. Due to its similarity to CDI processes, it is instructive to examine this technology from two perspectives. Firstly, it is a commercially accepted technology for water treatment. Secondly, there are commonalities between CDI and electrodialysis processes particularly with respect to ion transport in solution as well as through membranes that are worth noting and comparing. A critical review of electrodialysis separation technologies was written by Xu and Huang in 2008 [12]. In addition, Davis has written an excellent chapter concerning the electrodialysis process in Handbook of Industrial Membrane Technology [13].

### 3.2. The electrodialysis process

Electrodialysis involves moving ions in a potential field across polymeric anion and cation-exchange membranes. Shown in Fig. 5, is a pictorial illustration of the process. Cation- and anion-exchange membranes are placed alternatively between the cathode and the anode. When a potential difference is applied between both electrodes, the cations are drawn towards the cathode (negative electrode) and anions towards the anode (positive electrode). The cations migrate through the cation-exchange membranes, but are retained by the anion-exchange membranes. The opposite occurs with the anions that migrate through the anion-exchange membranes but not through the cation-exchange membranes. This movement produces a rise in the concentration of ions in some compartments (brine streams) and the decrease in the adjacent ones (dilute streams), from which purified water exits. As a result

**Table 2**
Total water cost for the major types of desalination plants worldwide.

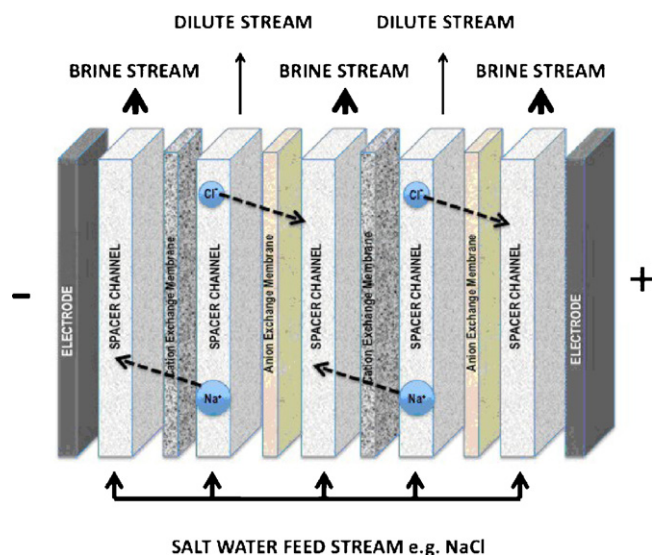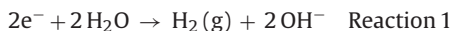| Type of cost | MSF | MED | RO |
|---|---|---|---|
| Thermal energy (M$) | 105 | 105 | 0 |
| Electric power (M$) | 92 | 76 | 114 |
| Operation and maintenance (M$) | 25 | 22 | 60 |
| Plant investment (M$) | 180 | 195 | 170 |
| Total cost (M$) | 402 | 398 | 344 |
| Water cost ($/m$^3$) | 0.52 | 0.52 | 0.45 |

**Fig. 5.** Schematic diagram of the electrodialysis process showing the migration of charged ions towards two charged electrodes.

of the anion and cation migration, electric current flows between the cathode and anode with equal charge equivalents transferred so that charge balance is maintained in each stream.
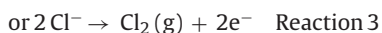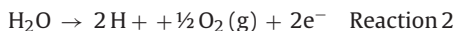
### 3.2.1. Electrode reactions

In electrodialysis, anode and cathode reactions may occur at each electrode depending upon the pH of the water and the potential applied.

At the cathode:

$$2e^- + 2H_2O \rightarrow H_2(g) + 2OH^- \quad \text{Reaction 1}$$

At the anode:

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2(g) + 2e^- \quad \text{Reaction 2}$$

$$\text{or } 2Cl^- \rightarrow Cl_2(g) + 2e^- \quad \text{Reaction 3}$$

In this process, hydrogen gas may be generated at the cathode and either oxygen or chlorine gas (depending upon the concentration of the electrode stream and the end ion exchange membrane arrangement) at the anode. The amount of gas evolved depends as well on the potential applied. These gases are subsequently dissipated as effluents from each electrode compartment and may be either combined to maintain a neutral pH or discharged. Alternatively, hydrogen gas may be used for other applications.

### 3.2.2. Energy consumption

In electrodialysis, the net energy consumption is the work applied to remove the dissolved ions from the solution:

$$W_{ED} = W_{deionization} = \frac{E_{deionization}}{\eta_d} = V\frac{I_m t}{\eta_d} \tag{1}$$

where $W$ is work, $E$ is energy, in Joules, $V$ is cell voltage, in V, $I_m$ is the minimum theoretical current necessary to remove a given amount of ions, in Amperes, $t$ is time, in s, and $\eta_d$ is the deionization or current efficiency, a measure of ion transport across the ion exchange membranes for a given applied current.

Additionally, the minimum theoretical current, $I_m$, is the product of the flow-rate times the change in concentration from the inlet to the outlet:
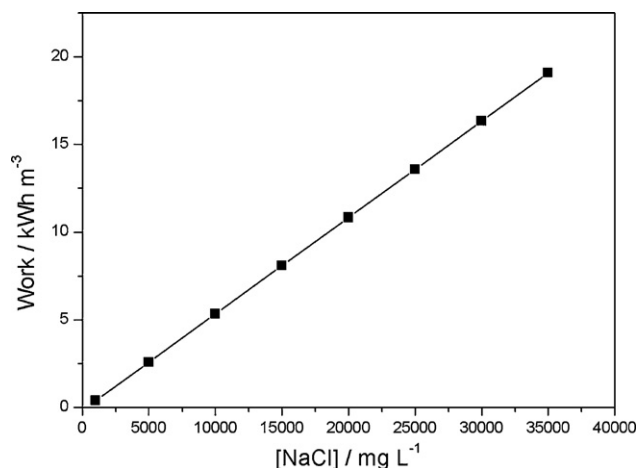
$$I_m = zFQ_f\Delta C \tag{2}$$



**Fig. 6.** Electrical work to produce $1\,m^3$ of a solution containing 0.3 g/L of NaCl as a function of the ion concentration at the inlet using electrodialysis. Operating cell voltage = 1.2 V, charge efficiency = 100%.

where $z$ = charge of the ion; $F$ = Faraday constant (96,485 Amp s/mol); $Q_f$ = diluent flow-rate, L/s; $\Delta C$ = change of ion concentration from inlet to outlet, mol/L.

Combining Eqs. (1) and (2) the net energy consumption is

$$W_{ED} = V\frac{zFQ_f\Delta Ct}{\eta_d} \tag{3}$$

Using Eq. (3) and taking $\eta_d = 1$, we have calculated the minimum theoretical work to produce $1\,m^3$ (0.27 kgal) of a solution containing 300 mg/L of NaCl from solutions of different concentrations. We have selected an operating cell voltage of 1.2 V. Results, plotted in Fig. 6, show that from a thermodynamic point of view, and even assuming efficiency of 100%, electrodialysis is not competitive with Reverse Osmosis when applied to solutions with ion concentrations beyond 2000–3000 mg/L.

Unfortunately, this is an ideal situation. Real current efficiency is always lower than 100%. However, it is important to note that current efficiencies higher than 80% are desirable in order to minimize energy costs. Low current efficiencies indicate: water splitting in the diluent or concentrate streams, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the diluent. Again, combining Eqs. (1) and (2), the following expression can be derived for current efficiency [14]:

$$\eta_d = \frac{I_m}{I} = \frac{zFQ_f\Delta C}{I} \tag{4}$$

where $I$ is the actual applied current, in Amperes.

It can be seen in Eq. (4) that the efficiency of the process is a direct function of the inlet feed concentration of ions. This can easily be understood as there are more charged species in more concentrated systems to carry current. However, from a practical point of view, one should also take into account that, due to concentration polarization at the membrane surfaces, a limiting current is reached [13]. In the brine compartments, the concentration is higher at the membrane surfaces than in the compartment bulk and in the diluted compartments the situation is reversed. The resistance to the flow of electric current increases as this interfacial concentration decreases. Net charge transport is related to the charge and the equivalent ionic conductance of charged species, anions and cations not necessarily being equivalent. Furthermore, charge transport in solution is different than charge transport through the exchange membranes (the later numbers are not generally available). For a complete description of this problem one should see the description offered by Davis [13]. Ortiz et al. have developed a mathematical model of a conventional electrodialysis process applied to the

desalination of brackish water [15]. The model allows one to predict the system's behavior under various operating conditions and to calculate the electrical energy consumption of commercial equipment.

### 3.3. Limitations of electrodialysis

Electrodialysis (ED) works best for removing low molecular weight charged species. The energy consumption of the ED system is proportional to the water salinity; thus, ED is more feasible when the salinity of the water is not higher than 6000 mg/L of dissolved solids. Also, the process is not suitable for water with a value of dissolved solids below 400 mg/L due to the low conductivity. Furthermore, comparatively larger membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions. As with RO, electrodialysis systems require feed pre-treatment to remove species that coat, precipitate onto, or otherwise "foul" the surface of the ion exchange membranes. However, electrodialysis reversal can minimize scaling by periodically reversing the polarity of the electrodes and/or the flows of the diluent and concentrate streams.

## 4. Capacitive deionization systems—a competitive energy efficient water treatment technology?

### 4.1. Background

As mentioned before, capacitive deionization (CDI), or as sometimes referred to as electro-sorption, operates using an applied potential, like its closest cousin, electrodialysis, to drive charged species (ions) to the electrodes. However, CDI does not involve membranes. It is therefore a low pressure process of deionization that has the possibility of directly competing with reverse osmosis or distillation as a means of delivering waters free of ions at reduced cost and operating expense [16–21]. CDI is an electrochemical process that operates by adsorbing ions in the double layer formed at the electrodes by the application of a potential difference. The principles of the process can be traced to the work of Helmholtz and to the modeling of the electrical double layer by Guoy–Chapman, as explained further below.

In a classic parallel plate capacitor, charge separation is electrostatic. Capacitance scales directly with the area of the plates and the inverse distance of separation as shown in Eq. (5):

$$C = \varepsilon_r \varepsilon_0 \frac{A}{D} \tag{5}$$

where $C$, is the capacitance in farads $F$; $A$ is the area of each plate in a traditional capacitor (usually metal) in square meters; $\varepsilon_r$ is the relative static permittivity (sometimes called the dielectric constant) of the material between the plates, (vacuum =1 F/m), $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12}$ F/m) and $D$ is the separation between the plates, in meters.

Capacitors can be connected either in parallel or in series, being the values of equivalent capacitance obtained by the following expressions:

$$\text{Parallel}: \quad C_{eq} = \Sigma C_n \tag{6}$$

$$\text{Series}: \quad \frac{1}{C_{eq}} = \Sigma \frac{1}{C_n} \tag{7}$$

The energy stored can be calculated by

$$E_{\text{stored}} = \frac{1}{2}CV^2 \tag{8}$$

where $E$ = energy in Joules; $C$ = capacitance in Farads, $V$ = potential difference in V.

#### 4.1.1. Double layer models

Due to factors such as surface polarization, adsorption of ions and orientation of polar molecules, the region between two different phases has a complex distribution of charge. This interface is known as double layer. Historically, there have been three models describing the double layer. The first model was proposed by Helmholtz in 1883 [22], and describes the distribution of charges at the double layer as in the case of a capacitor: surface accumulates charge of one sign while at the solution side the opposite sign charges are accumulated. A second model developed by Guoy–Chapman in 1913 already took into account the gradient of electron density at a charged interface, the so-called Thomas–Fermi screening distance, and its variation with distance from the surface. The consequence of this screening is that there exists a distribution of electric charge in the double layer region depending on the potential at the surface. In this model, other factors such as the Boltzmann distribution due to thermal effects (ions are not static) were also included. However, this model described ions as point charges. As a result, it predicted unrealistic high capacitance values due to extremely short distances. Lastly in 1924, Stern completed the model by assuming that the double layer can be divided in an "inner" region where ion distribution followed Langmuir's adsorption isotherm, while the region further from the surface could be roughly described with the Gouy–Chapman model. Thus, the total capacitance can be calculated like a series union of both, inner double layer (or Helmholtz's) and diffuse layer. For more detailed information the reader is addressed to Chapter 6 in Ref. [23].

#### 4.1.2. Zeta potential

Molecules, particles or ions in a solution form hydration shells that can also be described by means of double layer principles. Ions with a charge contrary to that of the surface will be highly attached to that surface, forming the inner or Stern layer, while those further away will form a diffuse layer. As a consequence, a potential difference between the surface of the particle, molecule or ion and that in the solution bulk is established. That parameter is known as electrokinetic (zeta) potential [24–27].

Zeta potential is an important and useful indicator of interfacial electrochemical character. For instance, it can be used to predict the stability of colloidal suspensions or emulsions, and its variation with parameters such as: conductivity, concentration, etc. However, the most important parameter affecting zeta potential for materials subsequently described in this paper is pH. The greater the zeta potential, the more likely the suspension is to be stable because two charged particles will repel each other and thus overcome the natural tendency to aggregate. A typical value of ±30 mV is considered to be the transition between stable and unstable suspensions, e.g. a suspension of particles with a zeta potential within those values would probably be unstable. The pH at which the zeta potential value is zero is called isoelectric pH, and would correspond to the least stable pH value for that suspension. The measurement of zeta potential is often the key to understanding dispersion and aggregation processes in applications as diverse as water purification, emulsions, paints, cosmetics, etc. We will show it to also be important to the CDI process.

The zeta potential is measured indirectly. When an electric field is applied, molecules, particles or ions will move through the solution together with all those ions (and polar molecules such as water) contained within its diffuse layer. The velocity of the particles moving towards the electrode when an electric field is applied is known as electrophoretic mobility, and constitutes the basis of a well known separation technique: electrophoresis. That velocity is influenced by factors such as the strength of the field, the viscosity and dielectric constant of the medium and the zeta potential, and
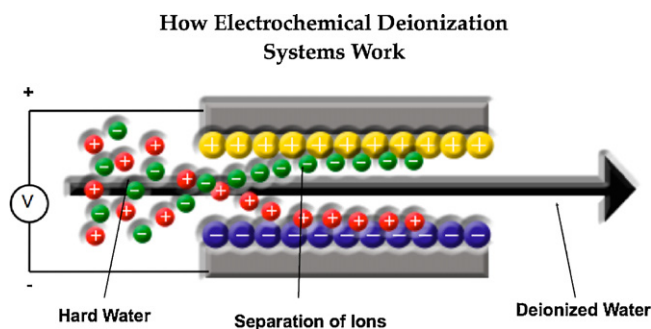
**How Electrochemical Deionization Systems Work**



**Fig. 7.** Schematic diagram of capacitive deionization showing the removal of charged ions or species by two charged electrodes.

is defined by the Henry Eq. (9):

$$U_e = \left( \frac{2\varepsilon\zeta f(k_a)}{3\mu} \right) \tag{9}$$

Being $U_e$ = electrophoretic mobility; $\varepsilon$ = dielectric constant; $\mu$ = viscosity, and $\zeta$ = zeta potential and $f(k_a)$ = Henry's function.

Thus, by measuring the velocity of the particles, by means of techniques such as laser Doppler electrophoresis, the value of zeta potential can be obtained.

### 4.2. The CDI process

CDI makes use of the above-mentioned basic capacitor principles to remove dissolved ions from an electrolyte (water) stream. In this case, the plates happen to be the electrochemical surfaces where ions adsorb following the principles of the double layer [9,28].

A representation of how the electro-sorption process works in the CDI system is shown in Fig. 7. Essentially, a solution of ions flows through a pair of electrodes and anions (or other negatively charged species) are retained at the anode (positive electrode) while the cations (or positively charged species) are separated from solution at the cathode. Ideally, no redox process occurs, and as a consequence the process is reversible and the electrochemical response is purely capacitive without any faradaic contribution.

Electrochemically, the capacitance of a CDI system can be evaluated by means of cyclic voltammetry. The potential window is constrained by the water redox potential values, typical operation values being 1.2–1.5 V. In absence of faradaic contributions, capacitance can be obtained directly from the voltammogram and sweep rate:

$$C = \int \frac{dq}{dV} = I \int \frac{dt}{dV} = \frac{I}{v} \tag{10}$$

where $q$ = charge in Coulombs, $V$ = potential difference in V, $t$ = time in s, $I$ = intensity (in Amperes), and $v$ = sweep rate in V s$^{-1}$.

The behavior of new electrode materials towards electro-adsorption could be directly obtained from resulting voltammograms. The more featureless and rectangular the curve the better, meaning that only capacitive processes take place without any contribution of faradaic (redox) reactions.

### 4.2.1. CDI history

A recent review of the CDI process directed specifically to the desalination community has been presented by Oren [29]. In this article, all of the fundamental aspects concerning the electro-adsorption process were exposed and therefore will not be examined in detail here. Historically, CDI dates back to the pioneering electrochemical demineralization work of the Caudle and Johnson groups in the late 1960s and early 1970s [30–32]. Oren also worked on his own version of CDI, which he referred to as

electrochemical parameter pumping [33,34]. During the late 1970s until the mid-1980s, Oren was the single largest advocate of the CDI process publishing papers on new carbon materials as well as fundamental electrochemical double layer aspects of electrodes [35–39]. However, a renewed interest in the CDI concept came in the mid-1990s when Farmer et al. [17–19] at Lawrence Livermore National Labs (LLNL), working on high surface area conducting carbon aerogels, developed their own version of a CDI device. The crucial aspect of these new materials was their large increase in surface area. As already stated, capacitance scales with surface area (Eq. (5)); thus high surface area carbon materials used as electrodes improve capacitance and have better performance with respect to electro-sorption. These high surface area materials have been essential in the development of both CDI devices and also electrical double layer (EDL) capacitors (sometimes called super or ultra capacitors). Both processes (EDL capacitors and CDI systems) operate in an identical fashion by adsorbing ions at a charged interface. Therefore, these aerogels and other similar high surface area conducting carbon materials can be used in both devices.

### 4.2.2. CDI energy considerations

In the case of capacitive deionization, provided that the energy stored in the capacitor can be easily recovered in the regeneration cycle, the net energy consumption is the difference between the energy supplied during deionization (charging of the capacitor) and the energy recovered during regeneration (discharging of capacitor):

$$W_{CDI} = W_{deionization} - W_{regeneration} = W_{charge} - W_{discharge} \tag{11}$$

Note that this equation is similar to that for electrodialysis (Eq. (1)) in which an additional subtractive term is included due to the fact that CDI systems actually store energy during the ion removal process; that energy can be recovered during the regeneration cycle. In principle, this would make the entire process more energetically favorable. However, some aspects such as efficiencies and irreversibility during the charging/discharging cycle must also be considered [9,28,40]. Unfortunately, until now, little effort has been expended upon developing electronic and electrochemical methods for performing regeneration effectively [29]. Since this task is an important and essential part of the CDI process, this energy savings strategy should be a major component of any working system.

On the other hand, some limitations of regeneration with respect to energy efficiency should be noted. Efficiency is defined [9] as the ratio between the amount of salt molecules removed from the solution and the amount of electronic charge transferred between the electrodes, in the charge–discharge cycle, for adsorbed ions into a highly porous surface. Biesheuvel [9] have described a thermodynamic model for the CDI process based in the GCS model including ion size constraints according to Carnahan-Starling equation of state. They obtain an analytical solution for charge efficiency concluding that efficiency only approaches unity by increasing cell voltage, Stern capacity or decreasing the ionic strength of the solution being treated. In this respect, attempts are being made to further evaluate the effect of these variables [40].

To understand the importance of the charge efficiency in CDI systems, we propose a macroscopic analysis based on the idea that the energy for deionization is equivalent to the energy stored in a capacitor, and the energy released during regeneration corresponds to the discharge of such capacitor. This energy is related to the work of charging and discharging the capacitor through the expressions:

$$E_{deionization} = E_{stored} = W_{charge}\eta_{charge} = \frac{W_{discharge}}{\eta_{discharge}} \tag{12}$$
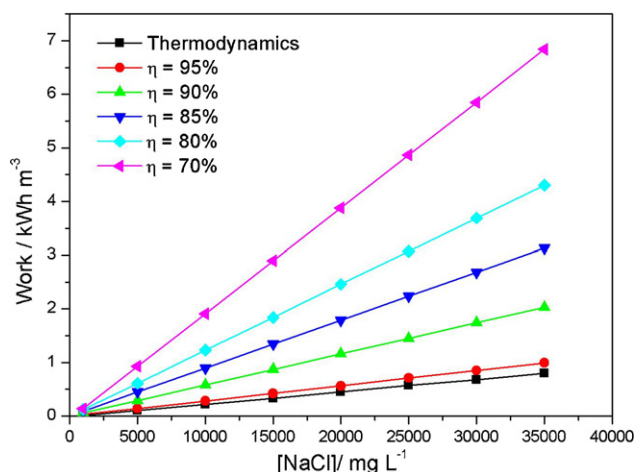
**Fig. 8.** Electrical work to produce 1 m$^3$ of a solution containing 0.3 g/L of NaCl from solutions of different concentrations using capacitive deionization (CDI). The operating cell voltage = 1.2 V, round trip efficiencies 70–95%.

As a consequence, the net energy consumption is related to the charge and discharge efficiencies by Eq. (13):

$$W_{CDI} = E_{deionization} \left( \frac{1}{\eta_{charge}} - \eta_{discharge} \right) \qquad (13)$$

Similarly to capacitors, the round trip efficiency can be calculated as the ratio between the work retrieved during the discharge of the capacitor to the work applied for charging:

$$\eta_{roundtrip} = \eta_{charge}\eta_{discharge} = \frac{W_{discharge}}{W_{charge}} \qquad (14)$$

Supercapacitors can show round trip efficiencies over 95% [41]. If a CDI device were to reach similar values, the practical application of CDI could be extended to a range of concentrations much wider than electrodialysis. We have made theoretical calculations for the work required to produce 1 m$^3$ of a solution containing 300 mg/L of NaCl from solutions of different concentrations (the same analysis as shown in Fig. 6), with an operating cell voltage of 1.2 V and round trip efficiencies ranging from 70 to 95%. Results are plotted in Fig. 8, where they are compared to the minimum thermodynamic work to remove such salts producing 1 m$^3$ of diluted solution and 0.25 m$^3$ of concentrated solution, calculated from the model described by Biesheuvel [9]. This model serves as a reference for calculating the maximum theoretical roundtrip efficiency, which in this case is around 96%.

Fig. 8 indicates that, under the selected conditions and at concentrations below 5000 mg/L, CDI could be a competitive technology even if moderate efficiencies, from 60 to 70%, are attained. Additionally, if efficiencies over 85% can be reached, CDI could become a serious competitor with RO, not only for brackish water, but for seawater desalination as well. Indeed Kötz and Carlen have reported round trip efficiencies of 92% for these type of supercapacitor electrodes [42], while Miller and Burke reported round trip efficiencies even higher than 95% [41].

In the original experiments of Farmer et al. [17,18], an energy consumption value of 0.1 kWh/m$^3$ was obtained for brackish waters. This number serves as a figure of merit or preliminary benchmark for this technology. However, Welgemoed and Schutte [21], using a larger pilot plant unit based on similar carbon aerogel CD materials, obtained a value of 0.6 kWh/m$^3$ to produce water with 500 mg/L of total dissolved salts from a 2000 mg/L synthetic solution. This value is considerably higher than the laboratory scale value obtained by Farmer et al. [17,18] although smaller than that obtained in the case of electrodialysis reverse systems
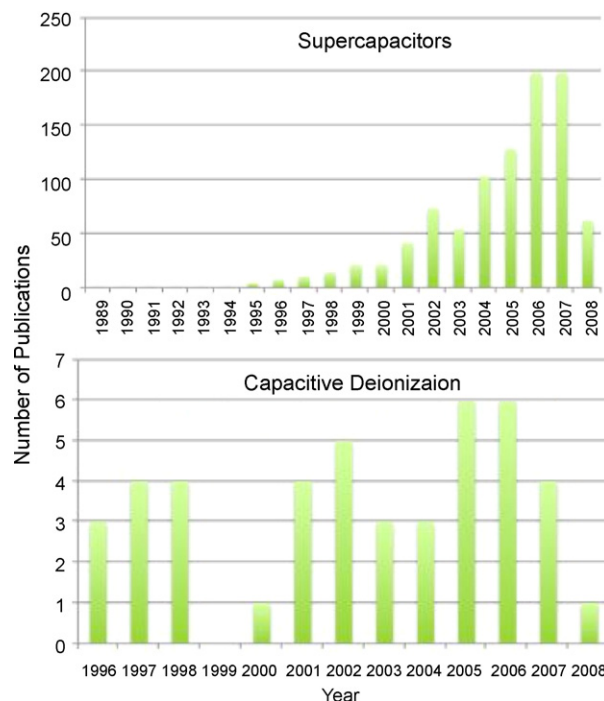


**Fig. 9.** Number of publications in supercapacitors and capacitive deionization along the last years.

(2.03 kWh/m$^3$) for desalination of brackish waters (AWWA M46, 1999 cited in [21]). In our theoretical analysis above, Farmer's results correspond to 90% roundtrip efficiency, while Welgemoed results are consistent with an efficiency of just 50%. Nevertheless, Welgemoed and Schutte [21] predicted that by including energy recovery during regeneration and by optimizing internal electrical connections, future industrial units could approach the laboratory scale energy consumptions.

### 4.3. Ultracapacitors in CDI systems for water treatment and energy storage

#### 4.3.1. Ultracapacitors for energy vs. CDI systems

In these days of water and energy shortage, it is interesting to remark that the same principle of charge sequestering at an interface, may be used to help solve both problems: delivering clean water and storing energy. Both fields are rather young. As seen in Fig. 9, interest in supercapacitor systems started to increase around the late 1980s but it was ten years later that more people started examining capacitive deionization systems. Unfortunately, it would seem that energy shortage is receiving the bulk of attention, as the number of papers being published per year in supercapacitor research is around 200 but only around 5–6 in the area of capacitive deionization. This situation may be changing since this past spring (2009) seven new papers have been devoted to CDI or electro-sorption processes [9,43–48]. Many of these papers are related to the use of new materials such as carbon nanotubes in the CDI process.

#### 4.3.2. Importance of electrolyte concentration and composition in CDI systems

The role of the electrolytes with respect to ion size, level of hydration and mobility in connection with pore size and pore connectivity is of high importance and many studies have been devoted to these issues [49–54]. Gabelich et al. [55] noted that, in spite of high surface area due to the presence of small pores (4–9 nm), only about 40 m$^2$/g was accessible to the ions, depending upon hydrated

ion radius. Li et al. [44] and Zou et al. [56] have more recently taken a fresh look at the subject of ion size using mesoporous carbon electrodes that are fabricated much in the same fashion as the famous ZSM-5 heterogeneous catalyst first patented by Mobil Oil in 1978 [57,58]. These materials have very small (<5 nm) regular pores. The authors suggest that not only pore size but pore regularity greatly influences electro-adsorption in these materials.

In brackish and seawaters, there are single valent cations present such as sodium, double valent ions such as calcium, and even triple valent ions such as iron. Anions are as well single and multivalent species having different levels of hydration. Gabelich et al. [55] remarked that CDI systems employing aerogel carbon electrodes present problems regarding multivalent ions removal due to size limitations. In the case of our own CDI system, we have not observed that problem [59].

It should be noted that the CDI process is not only dependent upon the composition of the ions present but also their concentration. Similar to that of ED systems, we can expect that as ionic strength increases, double layer distances collapse and surface potentials generated by the applied fields are shielded. This fact limits the total charge that can be stored at a given ionic strength and potential, which essentially corresponds to the maximum capacitance of the inner layer of the electrochemical double layer model [49]. This is thought to be one of the reasons why CDI methods of desalination may be more effective for brackish than for seawater scenarios [29]. However, by using asymmetric electrode materials having different pore size and differing charging mechanisms, it may be possible to improve the performance of CDI systems in waters having higher salt concentrations.

### 4.3.3. Carbon based CDI systems

Most current CDI or electro-adsorption systems typically utilize high surface carbon in a variety of forms. Many studies on CDI or electro-sorption utilize carbon aerogels [17,18,20,21,49,55,60–67], others use either carbon cloths [68–74], carbon sheets [75], carbon nanotubes [47] or carbon nanofibers [76–80]. Some carbons are deposited using a chemical vapor deposition process to reduce the size of the pores in carbon fiber electrodes [81]. Other carbon electrodes have been fabricated from carbon suspensions using a wet phase inversion method [43]. A simpler electrode can be fabricated simply by using pressed activated carbon granules or ordered mesoporous carbon synthesized by a modified sol–gel process [44,56,82]. A substantial review on carbon properties and their role from the point of view of its use in supercapacitors has been published in 2006 by Pandolfo and Hollenkamp [83].

A typical electrode pair configuration for carbon based CDI systems is shown in Fig. 10. As stated above, these systems became practical as a means of deionizing water only with the introduction of new materials—namely high surface area conducting carbons [17]. Important characteristics of electrodes in a CDI system together with capacitance and pore size distribution are range of stability with respect to applied potential and the stability of these electrodes in flowing aqueous media.

### 4.3.4. Other CD materials and our asymmetric system

It should be mentioned that other materials different from carbon can be used for CDI processes but examples are scarce. One exception has been the work of Bladergroen and Linkov [84]. These researchers studied electro-sorption using ceramic membranes. In our research group, we have also employed the concept of a ceramic membrane not as a mere separator between electrodes nor as a primary material of the electrodes, but rather as a thin-film nanoporous inorganic coating on the carbon fibers which changes the physical-chemical properties of the carbon [59]. A schematic of our CDI system is shown in Fig. 11. Indeed, as we shall discuss below, two asymmetric electrodes are used in this process. A different film
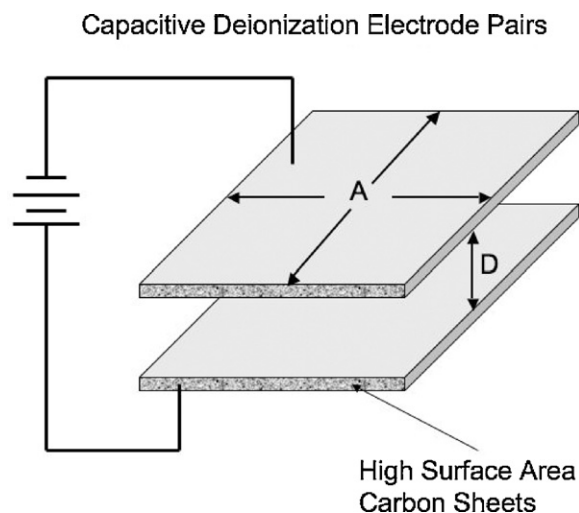
**Fig. 10.** Typical electrode pairs of carbon used in capacitive deionization.

covers each electrode. One electrode is coated with an acidic $SiO_2$ nanoporous film and the other with a basic $Al_2O_3$ nanoporous film. We refer to these asymmetric systems as fourth generation devices.

The main advantage of this sort of asymmetric system is the different intrinsic properties of each electrode. A distinct zeta potential exists for each material (electrode) at a given pH. This provides a superficial charge that is negative in the case of $SiO_2$ but positive in the $Al_2O_3$ film. Typically, seawater and drinking waters have a pH value between 7 and 8.5. As illustrated in Fig. 12, coatings on the carbon grid would be expected to be highly negative for the $SiO_2$ electrode and positive for an $Al_2O_3$ or Mg-doped $Al_2O_3$ electrode. That superficial charge will favour the electro-adsorption of cations or other positively charged species on the $SiO_2$ electrode. In contrast, anions or other negatively charged species are most likely to deposit at the Mg-doped $Al_2O_3$ electrode during the desalination process, but most importantly, it will avoid ions of the opposite charge to adsorb during the regeneration step, as will be discussed further below. However, we firstly introduce some concepts for an electrochemical analysis of deionization efficiency for this type of CDI system.
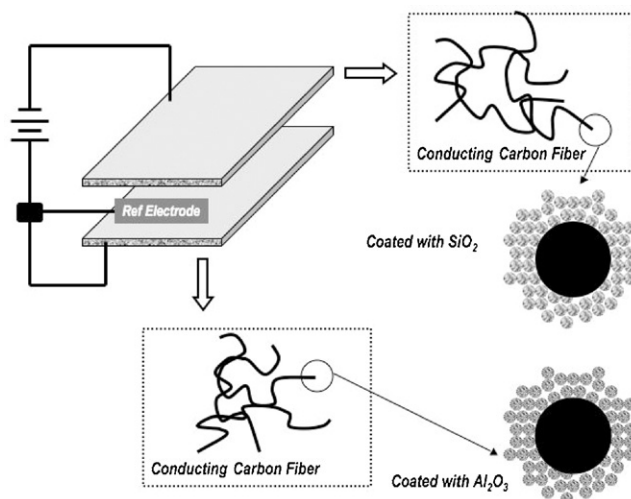
**Fig. 11.** Schematic diagram of our fourth generation CDI device showing the carbon fibers coated with different types of films.
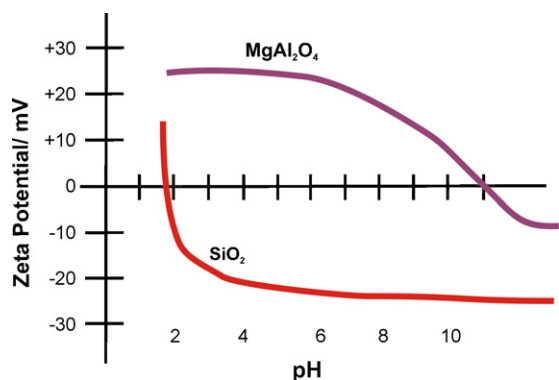
**Fig. 12.** Variation of zeta potential with pH for MgAl$_2$O$_4$ and SiO$_2$.

Deionization efficiency, $\eta_d$, is defined as the ratio between the charge injected to the electrodes and the amount of salt removed upon the cell polarization:

$$\eta_d = zF\frac{dn}{dq} \qquad (15)$$

Here $n$ is the amount of salt in moles removed from the bulk solution, $q$ is the amount of electrical charge (in Coulombs) added to the CDI cell and $F$ is the Faraday constant. This equation for capacitive deionization is essentially the same as Eq. (4) for Electrodialysis, provided that: $dn = Q_f\, dC\, dt$ and $dq = I\, dt$.

Efficiency of CDI systems depends on multiple variables; some of these variables are reviewed in the next paragraphs. One of them is redox process occurring on the surface of the electrodes such as water electrolysis. Such faradaic reactions begin to become significant only if a certain voltage level is exceeded, which can be viewed as a practical limit for electro-sorption processes. Below this threshold voltage, redox processes can be neglected unless electroactive dissolved species such as iron are present in the feed solution. The most relevant effect arises from the obvious fact that the electrolyte side of the electrical double layer is comprised of two types of charge carriers. Thus, electrical charge added to an electrode upon polarization is balanced not only by adsorbed counterions, which are opposite in sign to that of the electrical charge, but also by the desorption of the co-ions having the same charge sign as that of the electrical charge of the electrode. This is quantitatively expressed by Eq. (16):

$$dn = d\Gamma^- - d\Gamma^+ \qquad (16)$$

In which $d\Gamma^-$ and $d\Gamma^+$ are the infinitesimal changes in the surface molar excesses of anions and cations, respectively [40].

Combining Eqs. (15) and (16) we obtain:

$$\eta_d = zF\frac{d\Gamma^- - d\Gamma^+}{dq} \qquad (17)$$

According to the above equation, charge efficiency depends on adsorption of counterions and desorption of co-ions. This is particularly important if the electrode is at the potential of zero charge (PZC) where the amount of positive and negative charges adsorbed on its surface is the same, so the difference $d\Gamma^- - d\Gamma^+$ will be zero and $\eta_d = 0$. When the electrode is polarized, more counterions are adsorbed while co-ions are desorbed, so the efficiency will increase proportionally. When the amount of desorbed co-ions is zero, $\eta_d = 1$.

Some authors propose working at polarization voltages far from the PZC in order to maintain high charge efficiency [86]. However, this has the disadvantage of reducing the capacity of the electrodes to store charge. Furthermore, from a practical point of view, this option requires a fine voltage control of the device during regeneration, so as to avoid every electrode returning to its natural open circuit voltage.
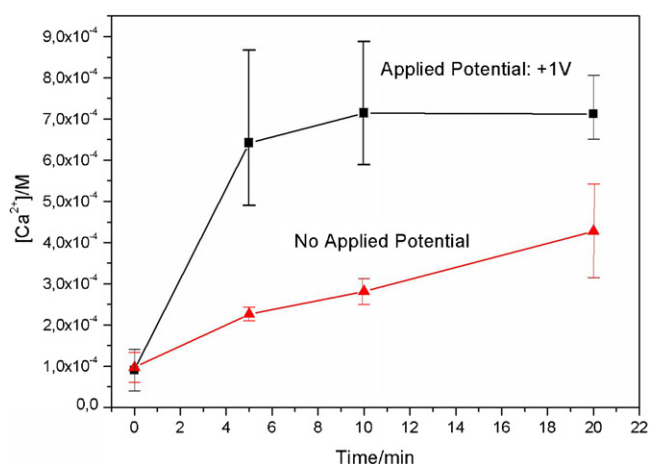


**Fig. 13.** Regeneration process of the 4th generation CD system using +1 V, pH 6.0 (black squares) and electrochemical regeneration using only diffusion (red triangles).

The alternative we have proposed is to modify the electrodes so that they spontaneously stay at zeta potentials far from the PZC. To obtain this condition, one of the electrodes must have a spontaneous positive charge and the other negative. Under these conditions, very few positive co-ions will be adsorbed on the positive electrode, nor negative co-ions on the negative electrode. Coatings using oxides having differing PZC's have been demonstrated to modify zeta potential of the electrode, without damaging their capacity. On the contrary, preliminary results show a moderate increase in their capacity to store electrical charges. Depending on the coating material zeta potentials can be positive or negative at the usual pH of brackish and seawater [59], so with an appropriate selection of coating materials the detrimental effect of co-ions on charge efficiency can be reduced without any external voltage regulation.

The contribution of our asymmetric system involving two materials with distinct and opposite surface potentials at the pH of seawaters and drinking waters allows us to regenerate electrodes more efficiently. Each electrode material has a given zeta potential at the pH of the solution that repels co-ions that are generated during the rinse cycle.

In Fig. 13, the concentration of Ca$^{2+}$ ions in the regenerating solution is shown. Without applying a potential, ions simply diffuse into solution (red triangles). However, if a reverse potential of 1 V is applied, we can regenerate the system to 75% of the initial Ca$^{2+}$ concentration in ten minutes (black squares) as compared to a 25% regeneration level relying on diffusion only. This increase in regeneration rates by applying a reverse potential substantially reduces the amount of waste brines produced in this process.

### 4.4. Devices and operational aspects of CDI systems

In the previous sections, we have shown the importance of materials for building cells with stable and optimal performances. However, when real life devices are conceived, we also need to consider operational aspects of these systems. Appropriate designs for the complete CDI system as well as sensible process engineering are needed for the implementation of this technology for specific applications. Some of what we consider relevant operational aspects of the CDI technology are discussed below.

#### 4.4.1. Two units in parallel

In order to advantageously utilize energy stored in a CDI unit, once its electrodes are fully charged, it is necessary to implement an electrical load that could allow discharging of such a unit. For our
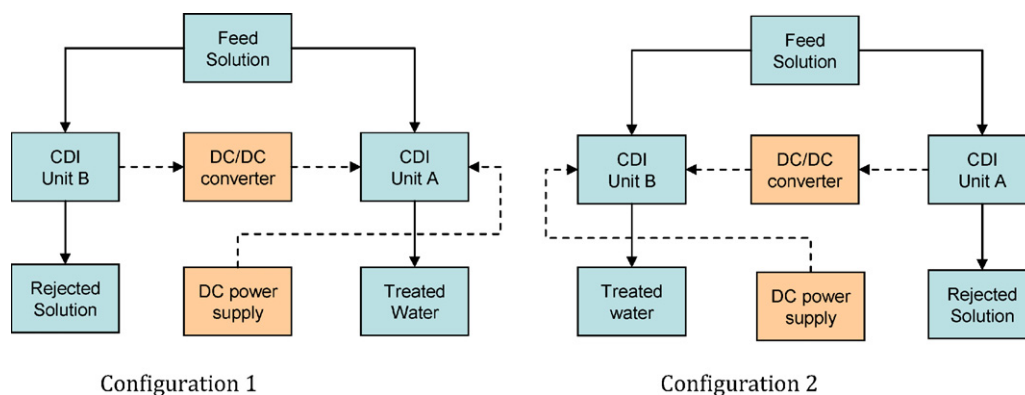
**Fig. 14.** Schematic drawing of the charge/discharge configurations. In configuration 1, the CDI Unit A is in the deionization cycle producing a diluted solution and Unit B is in the regeneration cycle discharging the adsorbed ions to the concentrate solution. In configuration 2, the situation is reversed.

CDI system we propose a second CDI unit working in parallel with the first, so when the first is regenerated, the energy stored can be applied to deionize the solution stream passing through the second unit. Once the second unit is saturated, the system will be reverted and the energy stored used to deionize a feed solution passing through the first CDI unit. This procedure is schematically depicted in Fig. 14. Energy stored in the CDI unit at the end of its deionization cycle will be delivered exactly as in the discharge of a capacitor. Such discharge will follow the typical *V–I* curve of any capacitor, which means that there is more or less a linear decrease of voltage with current or current density. However, charging a capacitor, in other words feeding the CDI unit during the deionization cycle, shall preferably be performed at constant current or constant voltage. In order to match two CDI units, one in regeneration and the other in deionization cycle, a DC/DC converter shall be placed in between. Such converter will transform the variable *V–I* curve of the CDI unit in regeneration cycle (discharge) into a constant current or constant voltage supply for the CDI unit in deionization cycle (charge).

In configuration 1, the CDI Unit A is in the deionization cycle using the energy stored in Unit B with the help of an external power source. Unit B is in the regeneration cycle discharging the adsorbed ions to the rejected solution while supplying DC power to Unit A. In configuration 2, CDI Unit A is in the regeneration mode while Unit B is in the deionization cycle and being fed with the energy stored in Unit A in addition to the external power supply.

### 4.4.2. Recycle loop

Very often, water treatment systems are designed for batch operation because these systems are easier to construct and usually require a lower investment. However, batch systems have operational drawbacks. A major issue is the fact that solution concentrations vary with time. At the beginning of the batch deionization cycle, the ion concentration is that of the feed solution, while at the end of the cycle the composition of the solution is mostly that of a dilute solution. In most cases, there will be remarkable changes in the physicochemical properties of the solution such as pH, conductivity, density and viscosity. Such changes require continuous adjustment of critical operating parameters such as current density and pumping or agitation power. In addition, the CDI cells, particularly the electrode materials, have to be stable over a wide range of working conditions.

To overcome these problems one needs to design a continuous operational system. This is based on recycling the outlet flux of the CDI unit to its inlet and coupling this with a make up of feed solution and a bleed from the solution to be treated. A schematic diagram of this system is shown in Fig. 15.

Although there is no doubt that this system is more complex than that of a batch system, its operation is easier because it is possible to adjust the concentration gap between inlet and outlet streams to a selected value simply by changing the ratio between the flow-rates of the recycle and bleed streams. At high recycle to feed ratio, the concentration in the unit remains almost constant. This allows one to operate under constant physicochemical parameters.

Another important feature of this system is that the actual operating concentration of salts within the CDI unit is very close to the concentration of the deionized product and independent of the concentration of the feed solution. Under these conditions, the efficiency remains rather constant and, more importantly, will always be kept near its maximum value for each specific application; keeping in mind that lower concentrations provide higher charge efficiencies [29].
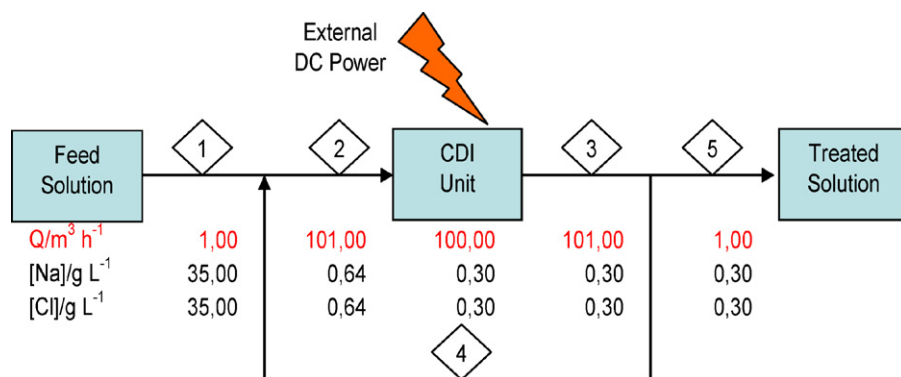


**Fig. 15.** Block diagram showing a continuous mode of operation. Feed solution of 35 g/L NaCl, treated solution of 0.3 g/L and $Q_{recycle}/Q_{bleed} = 100$.

## 5. Conclusions and future trends for CDI systems

In order for CDI systems to function at water treatment levels of millions of gallon per day (MGD) (hundreds of thousands of cubic meters per day), pairs of electrodes must be coupled into stacks and stacks into modules. To the best of our knowledge, the largest CD stack tested and reported in the open scientific literature has been in the study of Welgemoed and Schutte [21]. He experienced particular problems with the corrosion of stainless steel bus connectors for carrying current from the potentiostat to the conducting carbon electrodes. These problems were later resolved by using graphite bus connectors. The CDT$^{TM}$ patent of LLNL regarding the Resorcinol Formaldehyde (RF) based carbon aerogel [17–20] has been licensed by CDT technologies of Addison, TX. They have also licensed a newer porous carbon obtained from carbohydrates (TDA Research, Inc. (TDA), of Wheat Ridge, Colorado).

While problems of market penetration of CDI technologies may relate to the youth of the process, there are some other factors as yet to be resolved. One of these issues is related to the cost of materials. Much like supercapacitors, the cost of carbon needs to be reduced and the materials must prove to be stable over time and use. Several companies are playing in this sector but one company, Reticle [87], claims to have superior carbon for CD applications at reduced cost. There are additional problems related to regeneration rates, fouling and long-term stability that have not been adequately addressed until this time. To the best of our knowledge studies reported above by Welgemoed and Schutte [21] and that of Gabelich et al. [55] have begun to examine some of these problems in detail.

Fouling is of great concern for RO systems and as suggested by Oren [29], CDI systems may also suffer from this problem in actual operation. However, there is a significant advantage to the CDI process in this aspect as it has been shown that, by switching potentials of electrodes in electrochemical systems, one drastically reduces fouling [88]. Lastly, it is conceivable to apply a pulsed field to the electrodes to reduce both inorganic and organic fouling [89]. Fouling is a problem in all water treatment scenarios and particularly in membrane based systems. In the case of CDI systems, some controversy arises regarding this aspect. While Andelman [90] has theoretically provided a CDI system that claims to overcome these fouling problems from a design perspective, Oren has suggested that there is little practical evidence in the real world that this in fact works effectively [29]. On the other hand, Xu et al. [67], working on the treatment of brackish waters, have indicated that CDI systems are relatively free of fouling problems. Likely, this will remain the subject of further and longer term studies.

Finally, a couple of remarks concerning the benefits of CDI systems over that of RO and CDF desalination are worth mentioning. CDI is a low pressure process and is therefore expected, at least for brackish waters, to consume 1/3 less energy [91]. However, as we noted above, these CDI systems are performing as supercapacitors and therefore, while they are cleaning water they are also storing energy. We can recover much of this energy so that figures of merit mentioned above will improve. In addition, we may not always need to deliver the quality of water that RO and CDF provide. In situations such as coal bed methane recovery or the treatment of other brackish waters where CDI systems could be used to obtain water suitable to irrigate croplands [91].

The reader is reminded that this is a review paper as it examines the present state of art and past history of the CDI process in comparison to what we presently know about competing desalination systems. We are aware that in this review we have omitted some practical aspects with remarkable effects on capital and operational costs of these CDI systems. At the present time, there is a paucity of data on these systems with respect to the design of flow conditions inside CDI units, as well as regarding the power electronics or control logics needed to support these systems. Some of these important issues are now being investigated in some research and development projects that are currently in progress both at IMDEA Energy and at the University of Wisconsin in Madison.

The CDI technology is young and needs testing. As Oren [29] reminds us, there are only a few companies trying to commercialize this technology. While some results of these early commercialization stories seem to look promising, no information can be obtained on the length of field-testing, or how the electrodes behaved after longer periods of operation. More work remains, however, we should remember the pioneering work of Loeb and Sourirajan on RO membranes [8]. Their work on new materials made present-day reverse osmosis of seawater possible. Perhaps new electrode materials and better process control strategies will make this true for CDI. One hopes that we can recover our water resources and save energy as well.

## References

[1] C.A.S. Hall, J.W. Day, Am. Sci. 97 (2009) 230.
[2] R. Semiat, Environ. Sci. Technol. 42 (2008) 8193.
[3] M.E. Webber, Earth 3.0 (2008). http://www.sciam.com/article.cfm?id=the-future-of-fuel&page=5.
[4] S. Tully, Fortune Magazine 141 (2000) 342.
[5] M. Black, The No-nonsense Guide to Water, New Internationalist, Oxford, 2004.
[6] R. Borsani, S. Rebagliati, Desalination 182 (2005) 29.
[7] S. Chaudhry, CA Desalination Task Force Sausalito, CA (2003) http://www.owue.water.ca.gov/recycle/desal/Docs/UnitCostDesalination.pdf.
[8] S. Loeb, S. Sourirajan, U.S. Patent 3,133,132 (1964).
[9] P.M. Biesheuvel, J. Colloid Interface Sci. 332 (2009) 258.
[10] K.S. Spiegler, Y.M. El-Sayed, Desalination 134 (2001) 109.
[11] I.C. Karagiannis, P.G. Soldatos, Desalination 223 (2008) 448.
[12] T. Xu, C. Huang, AIChE J. 54 (2008) 3147.
[13] T.A. Davis, in: M.C. Porter (Ed.), Handbook of Industrial Membrane Technology, Noyes, Park Ridge, NJ, 1990.
[14] K.S. Spiegler, D.K. Laird, Principles of Desalination, 2nd ed., Academic Press, New York, 1980.
[15] J.M. Ortiz, J.A. Sotoca, E. Expósito, F. Gallud, V. García-García, V. Montiel, A. Aldaz, J. Membr. Sci. 252 (2005) 65.
[16] Q. Daoduo, Z. Linda, H. Eric, Res. J. Chem. Environ. 11 (2007) 92.
[17] J. Farmer, D. Fix, G. Mack, R. Pekala, J. Poco, J. Appl. Electrochem. 26 (1996) 1007.
[18] J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala, J.F. Poco, J. Electrochem. Soc. 143 (1996) 159.
[19] J.C. Farmer, S.M. Bahowick, J.E. Harrar, D.V. Fix, R.E. Martinelli, A.K. Vu, K.L. Carroll, Energy Fuels 11 (1997) 337.
[20] R.W. Pekala, J.C. Farmer, C.T. Alviso, T.D. Tran, S.T. Mayer, J.M. Miller, B. Dunn, J. Non-Cryst. Solids 225 (1998) 74.
[21] T.J. Welgemoed, C.F. Schutte, Desalination 183 (2005) 327.
[22] Helmholtz, J. Franklin Inst. 115 (1883) 310.
[23] J.O. Bockris, A.K.N. Reddy, M. Gamboa-Aldeco, Modern Electrochemistry, 2nd ed., Kluwer Academic/Plenum Publishers, 2000.
[24] M. Elimelech, J. Gregory, X. Jia, R.A. Williams, J. Gregory, X. Jia, R.A. Williams, Particle Deposition and Aggregation, Butterworth-Heinemann, Woburn, 1995, Ch. 2.
[25] R.J. Hunter, Zeta Potential in Colloid Science: Principles and Applications, Academic Press, London, 1981.
[26] J.J. Lyklema (Ed.), Fundamentals of Interface and Colloid Science Solid–Liquid Interfaces, Academic Press, 1995, Ch. 4.
[27] L. Dongqing (Ed.), Interface Science and Technology Electrokinetics in Microfluidics, Elsevier, 2004, Ch. 10.
[28] P.M. Biesheuvel, B. van Limpt, A. van der Wal, J. Phys. Chem. C 113 (2009) 5636.
[29] Y. Oren, Desalination 228 (2008) 10.
[30] D.D. Caudle, T.H. Tucker, J.L. Cooper, B.B. Arnold, A. Papastamataki, Research Report Oklahoma University Research Institute, 1966.
[31] A.M. Johnson, J. Newman, J. Electrochem. Soc. 118 (1971) 510.
[32] A.M. Johnson, U.S. Patent, 3,755,135 (1973).
[33] Y. Oren, A. Soffer, J. Electrochem. Soc. 124 (1977) C121.
[34] Y. Oren, A. Soffer, J. Electrochem. Soc. 125 (1978) 869.
[35] Y. Oren, A. Soffer, J. Electroanal. Chem. 206 (1986) 101.
[36] Y. Oren, A. Soffer, J. Electrochem. Soc. 126 (1979) C330.
[37] Y. Oren, H. Tobias, A. Soffer, Bioelectrochem. Bioenerg. 11 (1983) 347.
[38] Y. Oren, H. Tobias, A. Soffer, J. Electroanal. Chem. 162 (1984) 87.
[39] Y. Oren, A. Soffer, J. Electroanal. Chem. 186 (1985) 63.
[40] E. Avraham, Y. Bouhadana, A. Soffer, D. Aurbach, J. Electrochem. Soc. 156 (2009) 95.
[41] J.M. Miller, A.F. Burke, Interface 17 (2008) 53.
[42] R. Kötz, M. Carlen, Electrochim. Acta 45 (2000) 2483.
[43] J.A. Lim, N.S. Park, J.S. Park, J.H. Choi, Desalination 238 (2009) 37.
[44] L. Li, L. Zou, H. Song, G. Morris, Carbon 47 (2009) 775.
[45] J.B. Lee, K.K. Park, S.W. Yoon, P.Y. Park, K.I. Park, C.W. Lee, Desalination 237 (2009) 155.

[46] O. Kitous, A. Cheikh, H. Lounici, H. Grib, A. Pauss, N. Mameri, J. Hazard. Mater. 161 (2009) 1035.
[47] Y. Gao, L. Pan, H. Li, Y. Zhang, Z. Zhang, Y. Chen, Z. Sun, Thin Solid Films 517 (2009) 1616.
[48] R. Chandrasekaran, M. Koh, A. Yamauchi, M. Ishikawa, Electrochemistry 77 (2009) 51.
[49] K.L. Yang, T.Y. Ying, S. Yiacoumi, C. Tsouris, E.S. Vittoratos, Langmuir 17 (2001) 1961.
[50] H. Chia-Hung, P. Taboada-Serrano, S. Yiacoumi, C. Tsouris, J. Chem. Phys. 128 (2008) 044705.
[51] B. Kastening, M. Heins, Electrochim. Acta 50 (2005) 2487.
[52] A. Alfarra, E. Frackowiak, F. Beguin, Electrochim. Acta 47 (2002) 1545.
[53] A. Seron, H. Benaddi, F. Beguin, E. Frackowiak, J.L. Bretelle, M.C. Thiry, T.J. Bandosz, J. Jagiello, J.A. Schwarz, Carbon 34 (1996) 481.
[54] B.E. Conway, Electrochim. Acta 40 (1995) 1501.
[55] C.J. Gabelich, T.D. Tran, I.H. Suffet, Environ. Sci. Technol. 36 (2002) 3010.
[56] L. Zou, L. Li, H. Song, G. Morris, Water Res. 42 (2008) 2340.
[57] F.G. Dwyer, P. Chu, in Mobile Oil Corporation N.Y., U.S. Patent 4,526,879 (1985).
[58] B.P. Pelrine, N.J. Trenton, in Mobile Oil Corporation N.Y., U.S. Patent 4,100,262 (1978).
[59] K.C. Leonard, J.R. Genthe, J.L. Sanfilippo, W.A. Zeltner, M.A. Anderson, Electrochim. Acta 54 (2009) 5286.
[60] H.H. Jung, S.W. Hwang, S.H. Hyun, L. Kang-Ho, G.T. Kim, Desalination 216 (2007) 377.
[61] C.M. Yang, W.H. Choi, B.K. Na, B.W. Cho, W.I. Cho, Desalination 174 (2005) 125.
[62] W.C. Li, H.Q. Hu, Y.D. Zhu, S.W. Zhu, New Carbon Mater. 20 (2005) 217.
[63] P. Ranamararia, N. Mohan, C. Rajagopal, B.S. Garg, J. Sci. Ind. Res. 63 (2004) 938.
[64] S.W. Hwang, S.H. Hyun, J. Non-Cryst. Solids 347 (2004) 238.
[65] T.Y. Ying, K.L. Yang, S. Yiacoumi, C. Tsouris, J. Colloid Interface Sci. 250 (2002) 18.
[66] L.W. Hrubesh, J. Non-Cryst. Solids 225 (1998) 335.
[67] P. Xu, J.E. Drewes, D. Heil, G. Wang, Water Res. 42 (2008) 2605.
[68] H.J. Ahn, J.H. Lee, Y. Jeong, J.H. Lee, C.S. Chi, H.J. Oh, Mater. Sci. Eng. A 449–451 (2007) 841.
[69] H.J. Oh, J.H. Lee, H.J. Ahn, Y. Jeong, Y.J. Kim, C.S. Chi, Thin Solid Films 515 (2006) 220.
[70] M.W. Ryoo, G. Seo, Water Res. 37 (2003) 1527.
[71] M.W. Ryoo, J.H. Kim, G. Seo, J. Colloid Interface Sci. 264 (2003) 414.
[72] B.E. Conway, E. Ayranci, H. Al-Maznai, Electrochim. Acta 47 (2001) 705.
[73] A. Afkhami, B.E. Conway, J. Colloid Interface Sci. 251 (2002) 248.
[74] E. Ayranci, B.E. Conway, J. Appl. Electrochem. 31 (2001) 257.
[75] K.K. Park, J.B. Lee, P.Y. Park, S.W. Yoon, J.S. Moon, H.M. Eum, C.W. Lee, Desalination 206 (2007) 86.
[76] X.Z. Wang, M.G. Li, Y.W. Chen, R.M. Cheng, S.M. Huang, L.K. Pan, Z. Sun, Electrochem. Solid-State Lett. 9 (2006) E23–E26.
[77] X.Z. Wang, M.G. Li, Y.W. Chen, R.M. Cheng, S.M. Huang, L.K. Pan, Z. Sun, Appl. Phys. Lett. 89 (2006) 053127.
[78] Y. Gao, L.K. Pan, Y.P. Zhang, Y.W. Chen, Z. Sun, Surf. Rev. Lett. 14 (2007) 1033.
[79] D. Zhang, L. Shi, J. Fang, K. Dai, J. Mater. Sci. 42 (2007) 2471.
[80] Y. Gao, H.B. Li, Z.J. Cheng, M.C. Zhang, Y.P. Zhang, Z.J. Zhang, Y.W. Chen, L.K. Pan, Z. Sun, Thin Solid Film 217 (2008) 1616.
[81] E. Avraham, B. Yaniv, A. Soffer, D. Aurbach, J. Phys. Chem. C 112 (2008) 7385.
[82] L. Zou, G. Morris, D. Qi, Desalination 225 (2008) 329.
[83] A.G. Pandolfo, A.F. Hollenkamp, J. Power Sources 157 (2006) 11.
[84] B.J. Bladergroen, V.M. Linkov, Sep. Purif. Technol. 25 (2001) 347.
[86] E. Avraham, M. Noked, Y. Bouhadana, A. Soffer, D. Aurbach, J. Electrochem. Soc. 156 (2009) 157.
[87] C.C. Nesbitt, J. Chem. Soc. Abstr. 224 (2002) U529.
[88] M.I. Kerwick, S.M. Reddy, A.H.L. Chamberlain, D.M. Holt, Electrochim. Acta 50 (2005) 5270.
[89] R.E. Perez-Roa, D.T. Tompkins, M. Paulose, C.A. Grimes, M.A. Anderson, D.R. Noguera, Biofouling 22 (2006) 383.
[90] M.A. Andelman, U.S. Patent 5,779,891 (1998).
[91] K. Christen, Environ. Sci. Technol. 40 (2006) 639.