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Capacitive deionization (CDI) for desalination and water treatment — past, present and future (a review)

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Abstract

Capacitive deionization (CDI) has attracted the interest of the community investigating water treatment technologies since the mid-1960s. The technology is based on the recognition that high-surface-area electrodes, when electrically charged, can quantitatively adsorb ionic components from water, thereby resulting in desalination. The article reviews the theoretical and technological background of CDI, the history of its development, and past and present attempts towards scaling up and commercialization. It also provides a critical review of the advantages and limitations of the technology. In addition, further research approaches necessary to render CDI a mature and competitive technology for the treatment of brackish and surface waters are outlined.

Keywords: Capacitive deionization (CDI); Capacitive deionization technology (CDT); Electronic water purification (EWP); Electrosorption

1. Introduction

Capacitive deionization (CDI) is an electrochemically controlled method for removing salt from aqueous solutions by taking advantage of the excess ions adsorbed in the electrical double layer region at an electrode-solution interface when the electrode is electrically charged by an external power supply. When the electrode has a high specific surface area, this excess may become significant in terms of number of grams of salt adsorbed on a unit weight of electrode material. This factor renders the electrodsorption process quantitative and attractive for water treatment.

Early studies on CDI date to the mid-1960s and the early 1970s. The concept was first introduced by Caudle et al. [1], who used porous carbon electrodes made of activated carbon powder in a flow-through mode for water desalination. Later, Johnson et al. [2] studied CDI as a

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reversible process. Their work combined parametric studies with investigations of the theoretical basis of CDI and of various electrode materials [2–5]. The intensive studies undertaken by the group of Johnson were eventually discontinued, mainly because of the instability of the electrodes, particularly the anode. However, a preliminary cost evaluation performed by Johnson's group showed that efficient, low-cost desalination based on this technology could indeed be achieved, provided that sufficiently stable high-surface area electrodes could be produced. Following this work, Johnson and Newman [4] published a comprehensive theoretical analysis of ion adsorption on porous electrodes. In the light of its importance, this work will be discussed at length below.

The pioneering works of the groups of Caudle and Johnson triggered an enormous amount of work with a fundamental orientation aimed at reaching an understanding of the basic factors governing CDI. This research was accompanied by studies directed at developing novel electrode materials for efficient CDI and small and semi-pilot-sized devices for desalination and water treatment. However, despite the vast amount of CDI-related activity that spanned more than half a century and the intensive worldwide activity devoted to developing technologies for creating new affordable water sources (e.g., seawater and brackish water desalination) and for water saving (e.g., municipal and industrial wastewater reclamation), CDI has not yet emerged from the laboratory or from the smallest pilot scale and demonstration units to become a valid and mature commercial technology.

The objectives of this article are: (1) to present the theoretical and technological basis for CDI; (2) to describe broadly the experimental and technological achievements in developing targeted electrode materials, modes of operation and process variations; (3) to describe past and present attempts towards scaling up and commercialization of CDI; (4) to provide a critical review of the advantages and limitations of CDI; and (5) to outline the future R&D activities that are necessary for making CDI a more mature technology.

2. Background

2.1. Electrosorption of ions on electrodes

At any interface between an electrolyte solution and another medium (a solid or an immiscible liquid phase), there exist regions with excess charge while the whole interfacial system is, of course, electrically neutral. The two sides of the interface that carry an excess of opposite electrical charge are described by the term "electrical double layer".

The interface properties and structure between an electronic conductor (electrode) and an aqueous electrolyte solution have been well documented, both by the thermodynamic approach and by widely accepted models such as the Gouy-Chapman-Stern theory [6]. According to the latter theory, the electrical capacity of the interface, C_T, is expressed as the sum of two capacitors in series, namely as:

$$\frac{1}{C_T} = \frac{1}{C_{M-H}} + \frac{1}{C_{H-S}} \quad (1)$$

where $C_{M\text{-}H}$ is the capacity of a "compact" double layer between the electrode surface, M, and the plane of closest approach for the ions, H [this plane is sometimes known as the outer Helmholtz plane (OHP)] and $C_{H\text{-}S}$ is the capacity of the "diffuse" double layer spanning from plane H into the electrolyte solution.

By treating ions as point charges and assuming an ideally polarized electrode (no electrochemical reactions, namely, no electron transfer through the interface) and the absence of ion adsorption associated with specific interactions, Gouy and Chapman calculated the dependence of

the excess charge, q on the potential at plan (H), ϕ_H, in z–z electrolyte solution of bulk concentration C_s as

$$q = \left(\frac{2RT\varepsilon C_s}{\pi}\right)^{1/2} \sinh\left(\frac{|z|\Im\phi_H}{2RT}\right) \quad (2)$$

The electrical capacity of the diffuse double layer is then obtained by differentiating Eq. (2) with respect to ϕ_H:

$$C_{H-S} = |z|\Im\left(\frac{\varepsilon C_s}{2RT\pi}\right)^{1/2} \cosh\left(\frac{|z|\Im\phi_H}{2RT}\right) \quad (3)$$

The excess charge distribution at the interface between a charged electrode-electrolyte solution according to the Gouy–Chapman–Stern model is described schematically in Fig. 1.

When two oppositely charged electrodes are in equilibrium with the same electrolyte solution, an excess of charge is built up at the interface near each of the electrodes. The spatial charge distribution between the electrodes will then be that given by the sum of the separate distributions, as shown schematically in Fig. 2.

As can be seen from Eq. (3), the diffuse double layer capacity varies as a function of $C_S^{1/2}$. Another peculiar outcome of this equation is the minimum capacity at $\phi_H = 0$ (the so-called "potential of zero charge"). Some typical values of experimental and calculated diffuse double layer capacities at the potential of zero charge as a function of solution concentration are given in Table 1. It is evident that the electrical capacity increases with increasing the solution concentration. In addition, there is a large discrepancy between the measured and the calculated capacity values, but an in-depth discussion of this point is beyond the scope of this article. Nevertheless, Table 1 shows that the specific electrical capacities can reach high values, as a result of the extremely short distances involved in both the

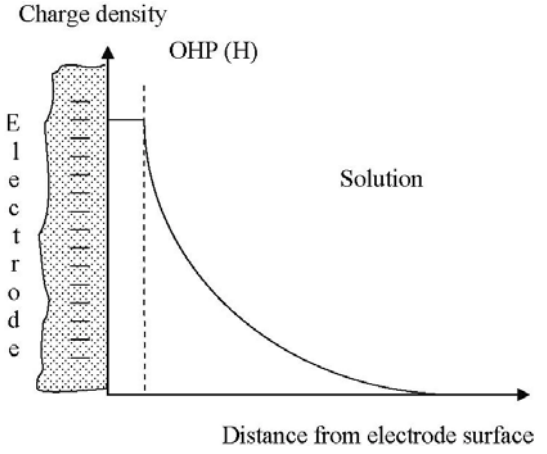

Fig. 1. Schematic representation of charge distribution in an electrolyte solution adjacent to a negatively charged electrode.

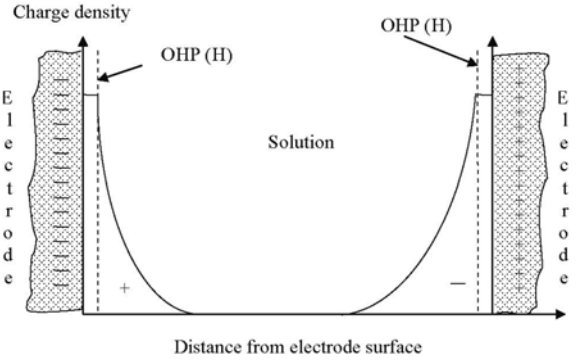

Fig. 2. Excess charge distribution in a two-electrode system (not to scale).

Table 1
Diffuse double layer capacity of Hg/NaF interface at the potential of zero charge

Concentration (N)	Diffuse double layer specific capacity ($\mu F\ cm^{-2}$)	
	Experimental	Calculated from Eq. (3)
0.001	6.0	7.2
0.01	13.1	22.8
0.1	20.7	72.2
1.0	25.7	228.0

Adapted from Bockris and Reddy [7].

compact and the diffuse double layer structures. These large specific capacities are important if the pair of electrodes is to function in CDI, as shown in the following simplistic calculation: Considering an electrode–solution system with a specific capacity of C_T= 10 μF cm^{-2} and assuming a voltage change of ΔV = 1 V, we would obtain a charge excess at the double layer region of $\Delta Q = \Delta V \times C_T$= 10 μcoulomb cm^{-2} or, in terms of equivalent ions, 1.036×10^{-10} equivalents cm^{-2}. This figure may appear quantitatively not practical for desalination. However, for a porous electrode (e.g. carbon) having a specific surface area of 1000 m^2 g^{-1} that is entirely accessible to ion penetration (an issue discussed below), it can be calculated that 1 g of this electrode material can adsorb an excess of 1.036 meq ions, a number that does appear promising for the desalination process. Thus, for two such electrodes, 50 g each would be required for the complete desalination of 1 L of 3000 ppm brackish water. Although this does not yet appear to be feasible for treating large water volumes because of the large quantities of electrode material required, there are several technological approaches to overcome this hurdle. These will be discussed below.

2.2. Analysis of desalting by charging a two-electrode system

Quantitative salt electrosorption on a pair of identical porous electrodes for CDI has been analyzed by Oren and Soffer [8–10] and by Johnson and Newman [4] who discussed in detail charge and energy efficiencies as well as adsorption/desorption kinetics, respectively.

The electrode pair separated by an electronically inert porous separator through which the salt solution flows has been described by an equivalent electrical circuit comprised of a network of electrical double layer capacitors, C_T, and electrical resistors R_M and R_S, representing the resistances of the electrode material and the solution, respectively, as shown in Fig. 3. Charging C_T by

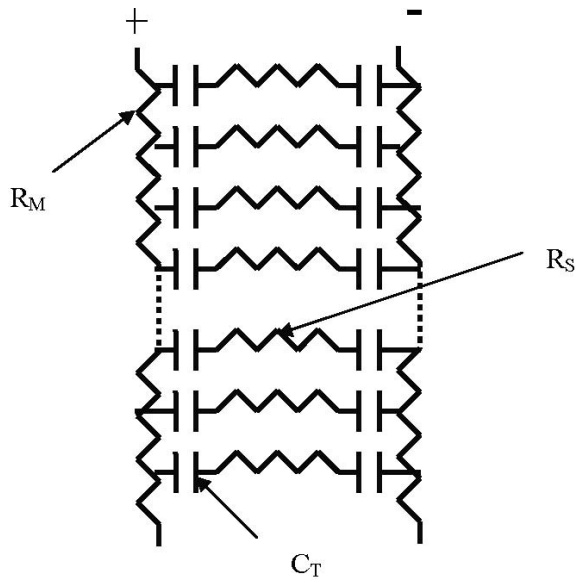

Fig. 3. Equivalent circuit representing a pair of charged electrodes.

increasing the potential of an electrode towards more positive values will result in an increase of anion adsorption and cation desorption. This is shown in Fig. 4, which presents typical anion and cation equilibrium adsorption curves on a single porous electrode. An electroadsorption cell comprising of two electrodes is operated by transferring an amount of charge Δq_e between the two electrodes. While anions are adsorbed on the positively charged electrode, they are desorbed from the negatively charged electrode. The same holds for the cations on the negatively and positively charged electrodes, respectively. The total amount of salt Δn_S adsorbed under equilibrium by the unit cell can thus be less than the charge equivalent $\Delta q_e/\mathfrak{F}$ exchanged between the electrodes. In some cases, the charge efficiency for adsorption $\mathfrak{F}\Delta n_S/\Delta q_e$ can reach a value of zero. Consequently, charge and energy efficiency parameters of a two-electrode cell may be derived by using single electrode characteristics [9]. As a first step, it is convenient to define q_e and q_d as new charge coordinates for the whole cell by the

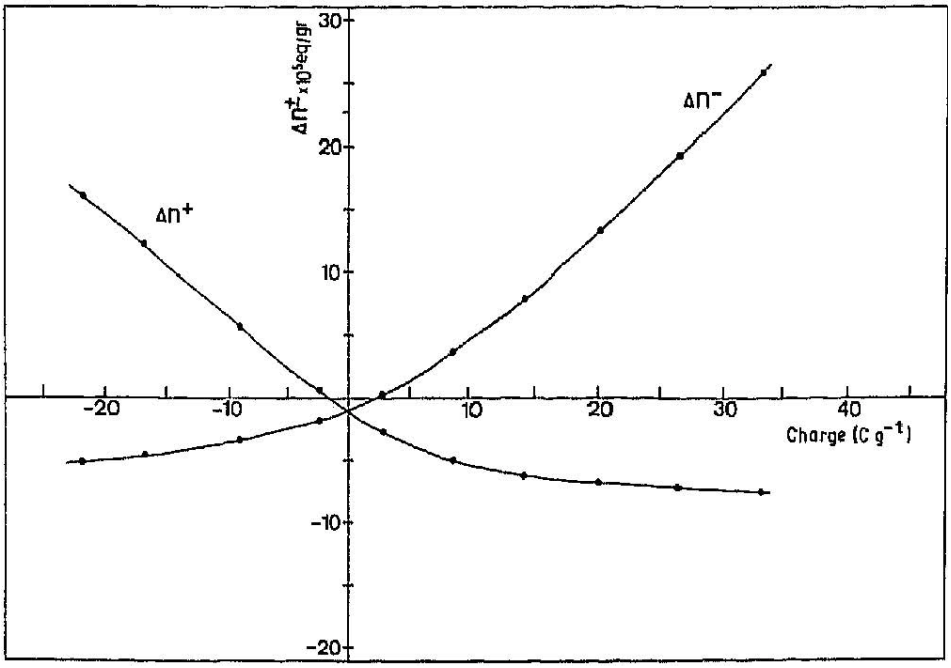

Fig. 4. Typical anion (Δn^-) and cation (Δn^+) excess adsorbed on a single FC-12 carbon electrode as a function of electrode charge. Solution: NaCl 0.12 M. (Reprinted with permission from the *Journal of Applied Electrochemistry* [9].)

properties of the individual electrodes 1 and 2 comprising the cell

$$\left.\begin{aligned} q_d &= \mu_1 q_1 + \mu_2 q_2 \\ 2q_e &= \mu_1 q_1 - \mu_2 q_2 \\ &\text{and} \\ \mu_1 &= g_1/(g_1+g_2), \mu_2 = g_2/(g_1+g_2) \end{aligned}\right\} \quad (4)$$

In the above expressions, q_1 and q_2 are the charges per unit weight and g_1 and g_2, the weights of electrodes 1 and 2 respectively.

From these definitions, it can be shown that q_d is the total cell charge, while Δq_e is, as noted above, the charge exchanged between the two electrodes. Both are calculated per unit weight of total electrode material. It should be noted that by exchanging $(g_1 + g_2)\Delta q_e$ coulombs between the two electrodes the total cell charge $(g_1+g_2)q_d$ does not change. It can be changed only by installing a third, auxiliary electrode within the cell through which electrode 1 or 2 can be charged independently. The average charge efficiency for a charging step of the system comprising two identical electrodes when charging from q_{e1} to q_{e2} is defined as:

$$\Im \frac{\Delta n_s}{\Delta q_e} = \frac{\Im}{q_{e2-}q_{e1}} \int_{q_{e1}}^{q_{e2}} \left(\frac{\partial n_s}{\partial q_e}\right)_{q_d} \mathrm{d}\, q_e \quad (5)$$

where $(\partial n_s/\partial q_e)$ is the differential charge efficiency at constant q_d.

The net salt charge adsorbed per unit of electrical charging work in the complete cell (the differential energy efficiency) is defined as $\Im(\partial n_s/\partial w)_{q_d}$, where w is the electrical work of charging the electrical double layer, namely,

$$\mathrm{d}\,w = \Delta E\,\mathrm{d}\,q_e = \left(\frac{q_e}{C_T}\right)\mathrm{d}\,q_e \tag{6a}$$

Accordingly,

$$\Im\left(\frac{\partial n_s}{\partial w}\right)_{q_d} = \Im\frac{C_T}{q_e}\left(\frac{\partial n_s}{\partial q_e}\right)_{q_d} \tag{6b}$$

The differential charge efficiency can be expressed by the individual charges as follows:

$$\Im\left(\frac{\partial n_s}{\partial q_e}\right)_{q_d} = \frac{\partial q_1^-}{\partial q_1} - \frac{\partial q_2^-}{\partial q_2} = \frac{\partial q_1^+}{\partial q_1} - \frac{\partial q_2^+}{\partial q_2} \tag{7}$$

At the extreme conditions, i.e., where electrodes 1 and 2 are highly positively and negatively charged, respectively, the following approximations hold:

$$\frac{\partial q_1^+}{\partial q_1} \approx 0;\ldots\frac{\partial q_1^-}{\partial q_1} \approx 1;\ldots\frac{\partial q_2^+}{\partial q_2} \approx 1;\ldots\frac{\partial q_2^+}{\partial q_2} \approx 0 \tag{8}$$

where q_1^-, q_2^-, q_1^+ and q_2^+, are the anion and cation excess charges on electrodes 1 and 2, respectively.

When these limiting values are inserted into Eq. (7), the efficiency approaches unity. Thus, for the two-electrode cell to approach its highest desalination capacity and differential energy efficiency, the electrodes should be maintained at the extreme opposite charge values.

The effect of the electrolyte concentration on the charge efficiency must also be taken into account. As the bulk concentration increases, the concentration of ions bearing the same charge as that of the electrode at the double layer region also increases. Therefore, ion depletion from that region is less likely. Consequently, charge efficiency may become lower at higher concentrations and may never reach unity.

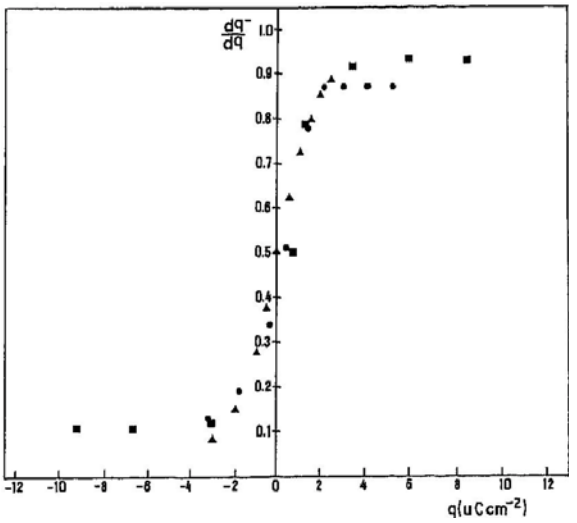

Fig. 5. Typical slopes $\partial q_i^-/\partial q_i$ vs. electrode charge q. ▲ FC-12 carbon electrodes; ● Gouy–Chapman–Stern model with ε = 20; ■ KF solution on mercury electrode. (Reprinted with permission from the *Journal of Applied Electrochemistry* [9].)

The charge efficiency ($\partial n_s/\partial q_e$) can be calculated from the single electrode properties provided that explicit expressions for $\partial q_i^+/\partial q_i$ and $\partial q_i^-/\partial q_i$ are known (such as that from the Gouy–Chapman model) or by using experimental data giving $\partial q_i^+/\partial q_i$ and $\partial q_i^-/\partial q_i$ as a function of the electrode charge or potential (Fig. 5).

By introducing the individual parts in Eq. (7) in terms of the Gouy–Chapman model and using the above charge coordinates, expression (9) follows:

$$\Im\frac{\partial n_s}{\partial q_e} = \frac{1}{2}\left\{\frac{Q_e + (Q_d/2)}{\left[\left(Q_e + Q_d/2\right)^2 + \mu_1^2\right]^{1/2}} + \frac{Q_e - (Q_d/2)}{\left[\left(Q_d/2 - Q_e\right)^2 + \mu_2^2\right]^{1/2}}\right\} \tag{9}$$

where $A = (2RT\varepsilon\varepsilon_0 C_S)^{1/2}$ in which $Q_d = q_d/2A$, $Q_e = q_e/2A$ where C_s is the bulk solution concentration.

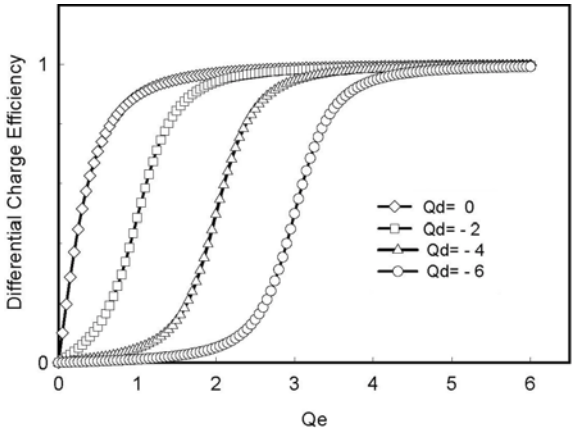

Fig. 6. Differential charge efficiency as a function of Q_e for different Q_d values.

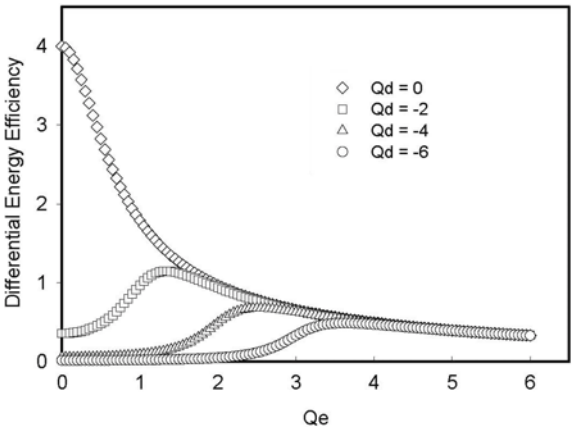

Fig. 7. Differential energy efficiency as a function of Q_e for different Q_d values.

The differential charge efficiency and the differential energy efficiency as derived from Eqs. (6) and (9) are shown as a function of Q_e for different Q_d values in Figs. 6 and 7, respectively. It is apparent that unlike the adsorption charge efficiency, the adsorption energy efficiency drops for high Q_e values and acquires maxima for intermediate values. This is due to the square power dependence of the capacitor energy on charge, while ion adsorption is, at most, proportional to the charge. For both efficiencies, the optimal values are obtained for $Q_d = 0$.

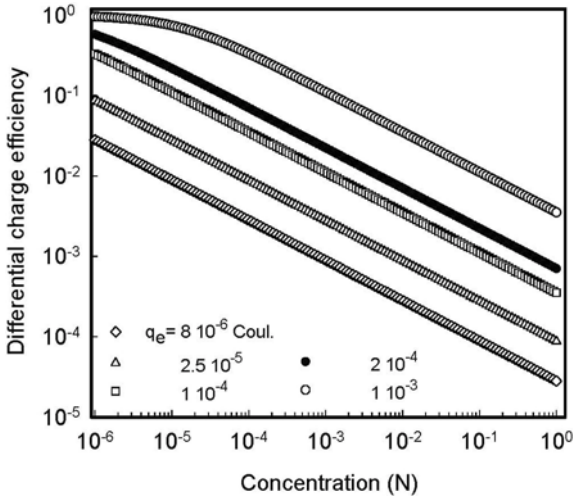

Fig. 8. Deferential charge efficiency as a function of solution concentration for different charge values, q_e and $q_d = 0$.

From the behavior of the two functions, the practical limits for q_d and the range q_{e1} to q_{e2} for attaining maximum efficiencies can be deduced: The total cell charge q_d should be as low as possible (practically, zero). The lower limit q_{e1} should be somewhat above zero, while the highest limit q_{e2} should be as large as possible, with the obvious limit being set by parasitic Faradaic processes such as water electrolysis. Furthermore, from Eq. (9) it can be shown that $\Im\left(\partial n_s / \partial q_e\right) \propto C_S^{-1/2}$, namely, the charge efficiency decreases as the bulk solution concentration increases, in accordance with the above discussion. This relationship is depicted in Fig. 8, which shows also that the differential charge efficiency decreases as the amount of charge Δq_e exchanged between the electrodes decreases. It should be pointed out that since the data in Fig. 8 were generated based on the Gouy–Chapman model equations and on the assumption that the electrodes are non-porous, the *absolute* numbers for the differential charge efficiency may be far from reality. However, the *relative change* of the differential charge efficiency with concentration may reflect the real situation quite well.

Johnson and Newman [4] analyzed the electrosorption kinetics of ions on porous electrodes in a two-electrode system. Taking into account that the adsorption rate is generally not rate determining, they found that while the capacity for electrosorption depends on the double layer electrical capacity, on the available surface area of the electrode and on the applied potential, the adsorption rate depends on the transport rate of charges to these surfaces and, hence, on the ohmic potential drop in the solution and the electrode matrix. Two characteristic times are associated with the process: For short charging times, the capacity of the electrodes is utilized only near the electrode separator and near the current collector. This time, τ_1 is expressed by

$$R_1 = \frac{2L}{\sigma + \kappa} + \frac{L_S}{\kappa} \tag{10}$$

where

$$\tau_1 = \left[\frac{R_1 (\kappa + \sigma) \kappa \sigma}{2\sqrt{\alpha}\left(\kappa^2 + \sigma^2\right)} \right]^2$$

where κ and σ are the specific conductivity of the solution and the electrode, respectively, α is the salt diffusivity, and L and L_S are half the thickness of the electrodes and the solution layer between them, respectively.

If the applied potential is maintained for a sufficient length of time, the entire electrode capacity will eventually be used up. The characteristic time, τ_2, for this is

$$\tau_2 = \frac{L^2}{\alpha} \tag{11}$$

Taking some ordinary values of the conductivities and diffusivity and reasonable values for the electrode and solution layer thicknesses (mm to fraction of mm), it was found that τ_1 and τ_2 have the characteristic order of seconds and hours, respectively. For a process based on the immediate availability of the surface electrical capacitance, τ_2 is extremely — and impractically — long. This issue is discussed further below.

In the above models, the porous structure of the high-surface-area electrode and its effect on the true capacity for ion adsorption was not considered explicitly. Lin et al. [11] and Yang et al. [12] pointed out that the surface area measured by traditional methods such as gas adsorption (BET using either N_2 or CO_2 as probes) and mercury intrusion porosimetry provide values that are much larger than those available for ion adsorption. A model was developed by Yang et al. [12] using the Gouy–Chapman–Stern theory for the double layer structure within a single cylindrical pore. Results for pore size distribution for a carbon aerogel (see below) were incorporated into the model equations, and experimental results on salt adsorption capacity as a function of bulk concentration and applied voltage were compared to the theory. It was concluded that only pores with diameter larger than a specific cutoff value really contribute to electrosorption of ions. The cut-off pore diameter reflects a maximum occupancy of the pore volume by the electrical double layer. The degree of occupancy is a function of the solution concentration and the applied voltage and full occupancy prevents ions from entering the pores, thereby lowering electrosorption capacity.

3. Technology development

Four main topics concerned with developing CDI into a commercially feasible technology for water treatment can be identified in the literature:

1. Development of an electrode material that is suitable for the process;
2. Arrangement of the various components within the basic cell unit;
3. Turning the process into a continuous or semi-continuous process; and
4. Energy recovery.

3.1. Electrode material

Following the discussion above, it is clear that the correct choice of electrode material is the most critical issue for the success of electrochemical separation processes, including CDI. A suitable CDI electrode material should have the following properties:

1. Specific surface area (i.e., the surface area per unit weight) available for electrosorption as large as possible;
2. Electronic conductivity as high as possible;
3. Fast response of the entire surface area to electrosorption–electrodesorption changes;
4. Chemical and electrochemical stability over a wide range of pH values and in the presence of oxidants (such as dissolved chlorine) and ability to tolerate frequent voltage changes;
5. Easily shaped according to design requirements;
6. Low propensity for scaling, biofouling and organic fouling.

In the light of these requirements, particularly the first one, it is not surprising that carbon—with its wide variety of available forms and porosity—has been found to be the electrode material of choice for CDI and other electroadsorption processes. The numerous studies dedicated to the fundamental electrochemical properties of carbon and graphite have shed light on the characteristics of the electrical double layer structure and its ability to quantitatively adsorb ions and on the effect of porous structure of the carbon electrode on the adsorption rate (e.g., Oren et al. [13]; Oren and Soffer [14,15]; Kinoshita [16]).

Among the various forms of carbon investigated for separation of electroactive materials by electroadsorption and CDI are activated carbon [17], activated carbon cloth [18], activated carbon cloth modified with titania [19,20], carbon felt [21,22], carbon black [8–10], sintered activated carbon [23], carbon nanotubes [24–26], and carbon aerogels [12,27–31]. The largest number of investigations has been devoted to carbon aerogels as the most promising available materials for this purpose. These unique porous materials consist of interconnected uniform particles, 3 to 30 nm in diameter, with interstitial pores that are less than 50 nm in diameter (Fig. 9). This type of structure gives high density and specific surface area in the range 400 to 1100 $m^2\ g^{-1}$, low hydraulic resistance, and an exceptionally high electrical conductivity of ~25–100 $S\ cm^{-1}$.

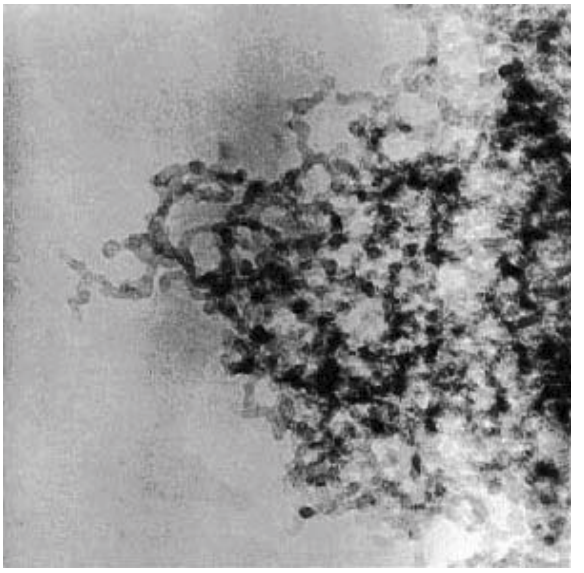

Fig. 9. Carbon aerogel microstructure: TEM visualization. ×500,000. Reprinted with permission from Galelich et al. [30] and *Environmental Science and Technology*.

Carbon aerogels are prepared by pyrolysing organic aerogels made from resorcinol-formaldehyde, phenol-furfural, phenol-resorcinol-formaldehyde, melamine-formaldehyde, polyurethanes, polyureas and polyvinyl chloride by the sol-gel process [32]. The organic aerogel porous precursor is prepared by polymerization of the relevant monomers into cross-linked polymer clusters forming wet gels. These gels are then dried before pyrolization under conditions that prevent the collapse of the porous structure, such as CO_2 supercritical drying [33] and solvent

exchange and controlled evaporation [34]. Pyrolysis is conducted at elevated temperatures (800–1100°C) at nitrogene atmosphere. The chemical composition, microstructure, and physical properties of the aerogels precursors can be controlled at the nanometer scale, giving rise to the unique electrical and electrochemical properties of the pyrolized material. Carbon aerogels can be prepared in the form of monoliths, powders, microspheres and thin film composites [27]. Pekala et al. [32], who were the first to prepare these materials, characterized their structure, properties and performance as electrodes for electrochemical separations in terms of the preparation conditions. They found that aerogel electrical capacitance is significantly influenced by the pyrolysis temperature and activation time, namely, in both cases it reaches a maximum with respect to these parameters. This implies that at sufficiently long activation times and sufficiently high temperatures the porous structure becomes partially closed, resulting in a decrease of the surface area.

As mentioned above, carbon aerogels are considered as promising materials for use in supercapacitors and in CDI and other separation processes based on electroadsorption [29,35–38]. The materials, their uses for different applications, and the methods of their preparation are covered by a series of patents held by the University of California and the USA DOE (e.g., [28,39–41]) and other bodies (e.g., [42,43]).

Carbon aerogel electrodes in the form of a CDI stack were tested by Farmer et al. [44,45] for the removal of Na_2SO_4, Na_3PO_4 and Na_2CO_3, from aqueous solutions and for removal of NaCl and $NaNO_3$ from single salt solutions. They also investigated the use of the same electrode stack for the removal of ammonium perchlorate from aqueous solutions originating from dissolving solid rocket propellants during decommissioning [45]. They found that the adsorption capacity for larger ions such as NO_3^- and ClO_4^- is lower than that for the smaller Cl^- ions. In addition, aging experiments showed that after a month of continuous operation the electrodes lost 6–8% of their adsorption capacity, particularly when operating at lower cell voltages. No explanation was given for this phenomenon, but this loss could be recovered almost entirely upon periodically reversing the electrode polarity [45].

Yang et al. [31] used carbon aerogel-silica composites for CDI. Silica was added in various proportions to the carbon matrix to improve the mechanical properties of the electrode, its ease of production, and its wettability. They showed that adding silica increased the electrode capacity by up to 28% resulting, as speculated by the authors, from increased wettability of the electrode material and, therefore, facilitating better accessibility to ions. An additional advantage was that preparation time of the electrode material was reduced by 50%.

Perhaps the most comprehensive study on the use of carbon aerogels in CDI under real conditions is that of Gabelich et al. [30]. They conducted a thorough study to elucidate the effect of ionic charge, radius and mass on the electrosorption of ions on carbon aerogels. A laboratory-scale CDI stack containing carbon aerogels that had been prepared under different conditions was used to separate salts from artificial single and multi-salt solutions. In addition, more complex streams of an unfiltered blend of 75% Colorado River water and 25% water from the California State Water Project, with and without small amounts of organic material, were studied so as to determine the effect of natural organic matter (NOM) on CDI performance. It was found that monovalent ions with smaller hydrated radii were preferentially removed from the solutions over multivalent ions. Two findings of practical importance emerged from this study: (1) Only a few percents (14–42 $m^2 g^{-1}$) of the BET electrode surface area (400–590 $m^2 g^{-1}$) were available for electrosorption; and (2) the presence of organic material in the treated water significantly reduced

the electrosorption capacity for ions, as a result of fouling of the aerogel surface and perhaps also the porous system. In water treatment applications, the two effects determine the overall adsorption capacity per unit volume of a CDI cell, as discussed further below.

Another type of electrode material was suggested by Gadkaree et al. [46]. They developed a family of high-surface-area carbon electrodes in honeycomb form. The technology is based on synthetic carbon precursors combined with a ceramic backbone that does not contain any binders. These structures contain up to 95% of carbon, which can then be activated to give surface areas in excess of 1000 $m^2\ g^{-1}$. The electrodes were optimized for ion electrosorption with respect to surface area and pore structure.

The point of fouling and scaling of CDI electrode was also addressed in the US patent of Andelman [23]. This patent makes claims for various CDI reactor configurations, including "washer-type", spiral-wound, "multiple manifold", flat type, "hexagonal road", that may potentially reduce the fouling propensity of the electrodes due to a reduced concentration polarization of the foulants as a result of an intensive mixing on the electrode surface. Electroadsorption in each configuration should be accompanied by polarity reversal of the electrodes in every charge cycle. However, although the patent claims for a foul-resistant flow through capacitor, it provides just a single example with a saturated $CaSO_4$ solution that does exhibit electrode scaling through precipitation. No discussion is provided on the possible adverse implication of organic and bio-fouling of the electrodes.

In summary, the following points should be emphasized:

1. Referring to the BET surface area of a porous electrode as the "true" surface area available for electrosorption of ions is misleading. In the BET analysis, a gas, usually nitrogen is used as a probe to measure pore size distribution including pores that are not penetrable by ions due to size differences. As a result, the BET surface area is much larger than that accessible by the hydrated ions, as clearly stated by Gabelich et al. [30]. As noted above, this reduces the specific electrosorption capacity, which is, in turn, reflected in the size of the CDI device.

2. The fact that hindered diffusion of ions into extremely small pores is involved, leads to decreasing rates of the electrosorption/desorption processes. This phenomenon becomes crucial when a cyclic, adsorption-regeneration procedure is considered.

3. Organic fouling, biofouling and scaling by sparingly soluble salts of the electrodes are discussed only superficially in the literature. As noted above, this is a critical issue when the treatment of "real" waters is considered. In the absence of reasonable solutions, these phenomena may render CDI prohibitive because of electrode blocking, leading to loss of electrosorption capacity and increase of energy consumption due to reduction of cell conductivity.

3.2. Design and modes of operation of CDI units

The first attempt to operate CDI in a pseudo-continuous mode was that of Oren and Soffer [8,10] in a process that was termed "electrochemical parametric pumping" due to its similarity to the previously developed cyclic "thermal parametric pumping" for separation of liquid mixtures [47]. The electrochemical parametric pumping column for the separation of salt from water consisted of two identical high-surface-area carbon black electrodes separated by an electrically inert porous barrier and filled with the appropriate solution. Each electrochemical parametric pumping cycle comprised four consecutive operations, as shown in Fig. 10:

- (A) *Adsorption*, which in a generalized sense is a step of transfer of material to be separated from the solution to the electrode phase,

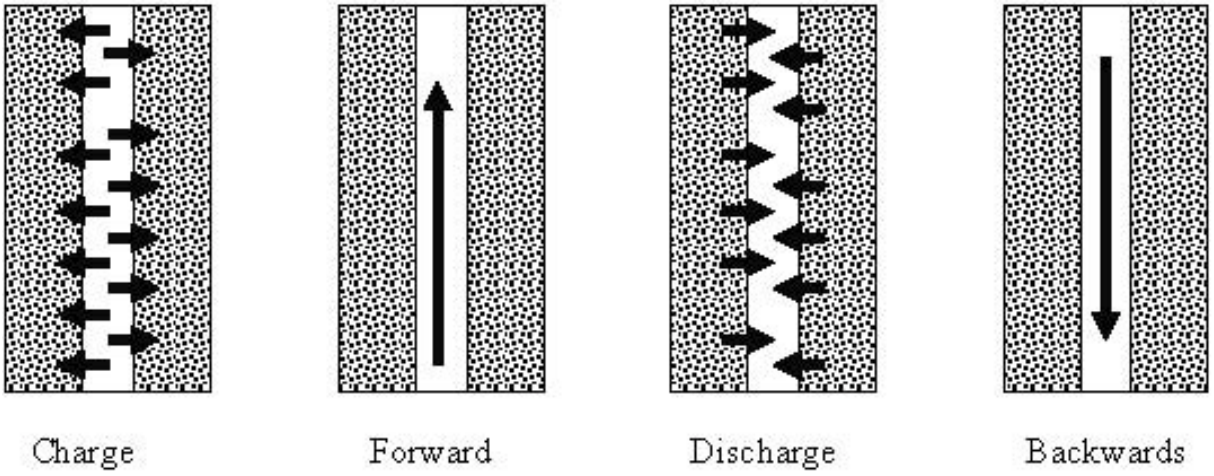

Fig. 10. Four basic stages of the electrochemical parametric pump. Reprinted with permission from the *Journal of the Electrochemical Society* [8].

which is induced by changing the potential difference across the electrodes;

- (B) *Forward axial pumping of the solution*, during which the salt bound to the electrodes remains stationary;
- (C) *Desorption*, which is also an electrically induced step that results in back transfer to the solution of exactly the same amount of salt that had been adsorbed onto the electrodes in the first step and;
- (D) *Backward axial pumping of the solution*, now containing an excess of salt.

In each cycle, the stream moving forward is poorer while the stream moving backwards is richer in the separated salt. In a multi-cycle operation, salt gradient is established along the electrode column while diluate and concentrate streams could be withdrawn from its ends.

In the studies of Oren and Soffer [10], the electrochemical parametric pump was operated fully automatically in two basic modes: total reflux and product withdrawal. Some typical results are presented in Fig. 11 for the two cases. In addition, two models for the build-up of the concentration profile within the column were elaborated. The first involved a solution of a two-phase mass transport equation with the proper boundary and initial conditions, while the second was based on the mixed-cells approximation. In

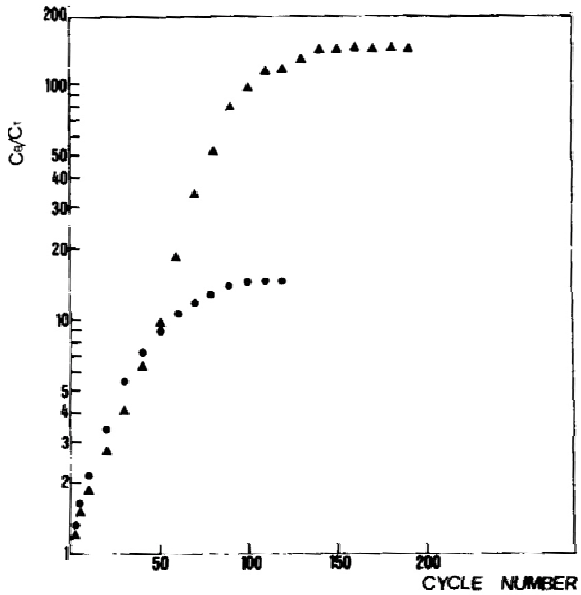

Fig. 11. Variation of the ratio between bottom (C_B) and top (C_T) concentrations as a function of number of cycles in an electrochemical parametric pumping column. Salt concentration 0.05 M, ●- $\Delta V/Vo = 0.5$, ▲- $\Delta V/Vo = 0.25$. ΔV and Vo are the volume step and column volume, respectively. Reprinted with permission from the *Journal of Applied Electrochemistry* [10].

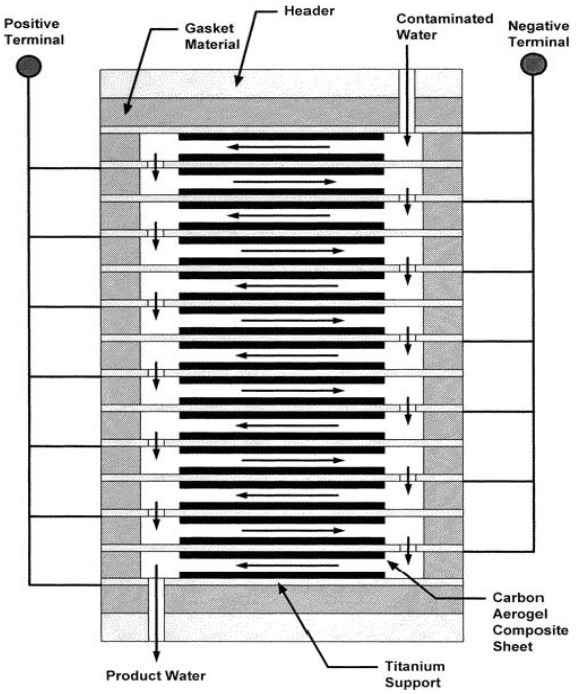

Fig. 12. Schematic representation of an electrochemical adsorption-regeneration cell. Reprinted with permission from Farmer et al. [48] and the American Chemical Society.

both cases, electrochemical equilibrium between the solution and the electrode surface was assumed. For both models, a computer algorithm was used to simulate the multi-cycle operation of the electrochemical parametric pump.

Following the above work, Farmer, Tran and their coworkers designed an electroseparation set-up based on carbon aerogel multiple electrode cells [28,48–50]. The electrochemical stack, shown schematically in Fig. 12, is composed of separated electrode pairs held together by a titanium frame, through which the treated solution flows in a serial manner. All the even-numbered electrodes are electrically connected, as are the odd-numbered electrodes. The two sets of electrodes are connected to an external power supply. The solution is desalted by polarizing the electrode pairs, and regeneration is accomplished by short-circuiting the electrodes. At the regeneration stage, the flow is discontinued, while the salt is desorbed from the electrodes. In this manner, the waste (concentrate) volume is minimized. An example of an adsorption-regeneration cycle is shown in Fig. 13. It is suggested that two CDI units be operated simultaneously, one unit to work in the adsorption mode while the other is being regenerated. In this way, pseudo-continuous operation is achieved.

Farmer [47] has listed some possible important applications of the separation process, including: Removal of various ions, including radionuclides from low-level radioactive wastes or from wastewater without the generation of acid, base, or other similar secondary wastes; treatment of boiler water in nuclear and fossil power plants; production of high-purity water for semiconductor processing; electrically driven water softening for homes (the CDI system softens drinking water without the need for sodium chloride and does not require salt additions for regeneration); removal of salt from water for agricultural irrigation; and desalination of seawater.

An interesting version of a pseudo-continuous CDI setup was suggested by Shiue et al. [51] in which two or more CDI units are installed in a two-compartment carousel (Fig. 14). One set of the CDI units is designated for deionization while the other set, for regeneration. As the carousel rotates, the CDI units switch positions and functions. An additional option is design for energy recovery, namely, while the deionizing CDI cells are charged by an external power supply, the regenerating cells release their residual electrical energy to an external accumulator for further use.

Shiue et al. [52] also filed a patent proposing a CDI unit (or a "flow through capacitor" as termed by them) in which the two electrodes are wound together with porous inert dividers in a concentric (spiral wound) manner. The electrode material comprises black magnetite (Fe_3O_4) nanoparticles, as the active material, attached to current collectors made of aluminum, copper,

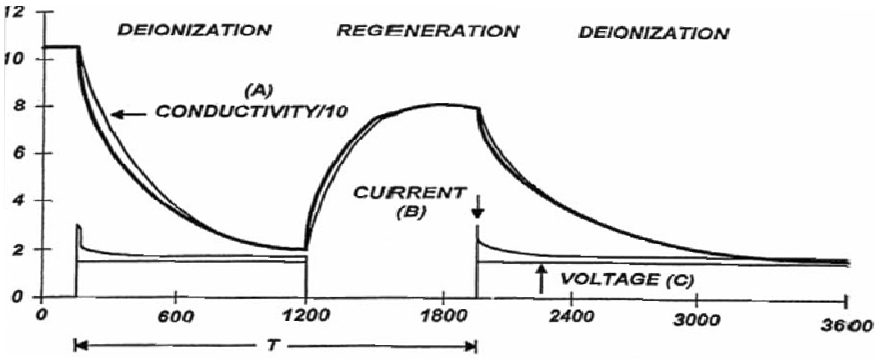

Fig. 13. Three superimposed (schematic) timing charts taken from the system shown in Fig. 12. Solution: NaCl, 100 μS cm^{-1}. A, electrolyte conductivity; B, cell current; C, cell voltage; T, deionization-regeneration cycle. Reprinted with permission from Farmer [47] and the US Patents Office.

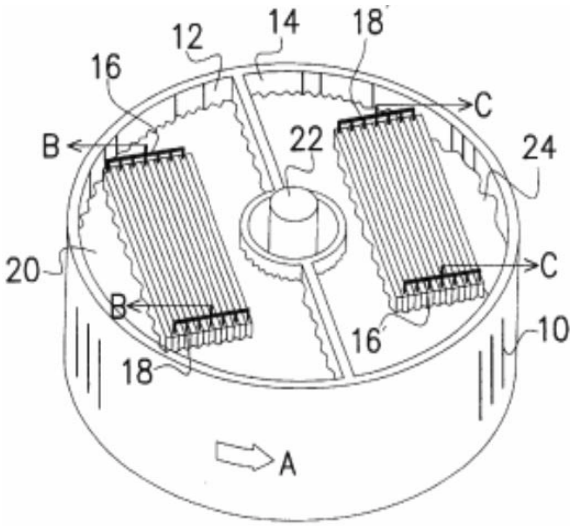

Fig. 14. Two CDI units in a carousel arrangement for deionization and energy recovery. Reprinted with permission from Shiue et al. [51] and the US Patents Office.

titanium, stainless steel or nickel foils. It is claimed that this arrangement is suitable for treating waste streams, water purification and desalination. However, no reference is given to the question of the stability of these electrodes and the possible contaminating potential.

3.3. Commercialization and case histories

The first attempts towards commercialization of CDI began between 1999 and 2000, when two US companies, Biosource, Inc. and Sabrex of Texas, Inc., were awarded a contract from the Defense Advanced Research Products Agency (DARPA) to develop a prototype portable water treatment unit based on CDI for the US Army. At the same time, the US Far West Group, Inc. (now Capacitive Deionization Technology Systems Inc.) received a development contract from Arizona Public Service (APS) to supply a CDI prototype [termed capacitive deionization technology (CDT)] for a water purification system for study by APS.

Based on the above activity, Sabrex launched the electronic water purifier (EWP), declaring it to be capable of removing dissolved ions, including iron, arsenic, chrome, perchlorate and nitrate, and of treating brackish, sea- and wastewaters. According to the developer, the unit is also suitable for use as home water purifier in conjunction with UV. However, no record could be found of the fate of the portable CDI unit for military use.

Recently, two other companies have declared achievements in CDI technology. ENPAR

Technologies Inc., located in Ontario, Canada, announced the shipping of a small-scale DesEL unit—a CDI-based technology—to the University of Montreal for testing by Anjou Recherche, the Research and Development Division of Veolia Environment, and CDT Systems, Inc., a Texas-based company, announced the launch of a mobile CDT System. Their technology is also presented in a document on new advanced technologies published by the Missile Defense Agency, Advanced Systems Technology Application Program (MDA/AS) (2004) as a technology suitable for water treatment in disaster areas. However, the commercialization status of the mobile unit was not made clear in the presentation. It should be mentioned that all the technologies mentioned above make use of a carbon aerogel as the electrode material.

Case histories are important since they show whether a technology is reliable under real operating conditions. The literature on case histories regarding CDI is somewhat limited and is restricted to the activity of ENPAR (DesEL) and a research group at Sandia NL [53].

ENPAR's experience covers the following water treatment cases:

1. *Nitrate removal from drinking water in a Middle Eastern country*. The main objective of the work was to adapt the DesEL technology for the selective removal of nitrate from a drinking water source with an average NO_3^- concentration of 155 mg L^{-1} while preserving the original taste of the water. The concentration of nitrate was reduced to less than 50 mg L^{-1} (which yet violates the US primary drinking water standards) and the TDS of the treated water was reduced from 787 mg L^{-1} to 512 mg L^{-1}, a value that approaches the USEPA secondary standard (aesthetic standard).

2. *High ammonia/nitrate contaminated groundwater at an industrial site in southwestern Ontario*. The DesEL system was found to be effective in removing ammonia-N and nitrate-N compounds to below the target level of 10 mg L^{-1} total nitrogen from initial concentrations of 500 and 270 mg L^{-1}, respectively. Water recoveries up to 95% were achieved using a multistage system.

3. *Intake process water at Hamilton Harbor*. The objective of the tests was to reduce the concentration of Ca to 40 mg L^{-1} and that of Cl^- to 60 mg L^{-1} in the water stream. The concentration of TDS in the treated water was decreased by more than 80%. The concentration of Ca was reduced by 90% from 55 mg L^{-1} to 5.4 mg L^{-1}, while that of Cl^- was reduced by more than 80% from 121 mg/L to 21 mg L^{-1}.

4. *City of Greater Sudbury, Lake Ramsey, Ontario*. The tested water sample represented typical surface water in the region, which may be used as a source of drinking water. Recovery of treated water was in excess of 90%, and the concentration of TDS was reduced by 92%. The waste stream represented less than 10% of volume of the input sample.

5. *Mine wastewater northern Quebec, Ontario, Canada*. A four-stage system was developed to recover up to 90% of the waste stream as clean water. The conductivity of the treated water was reduced from 30 mS cm^{-1} to less than 3.2 mS cm^{-1}.

The Sandia CDI experience is limited to the clean up of wastewater from coal-bed methane (CBM) production. This technology was used because it is considered to have potential for cleaning up the large volumes of brackish water extracted along with the natural gas. Sandia's laboratory tests used CBM water, with TDS levels of 2000–5000 ppm, which was generated in New Mexico's San Juan Basin, where much of the CBM development has occurred to date. Removal rates ranged from 75 to 90%, with the highest recoveries associated with the lowest TDS concentrations.

It should be stressed that although the cases described above appear promising, no infor-

mation was disclosed on the length of the tests or how the electrodes behaved at long operation times.

4. Discussion and conclusions

CDI could be potentially attractive for water treatment for the following reasons:

1. Unlike membrane-based treatment technologies such as reverse osmosis and nanofiltration, CDI does not require high pressures; thus equipment such as housing, pipes, and pumps is less costly.

2. CDI requires low voltages that normally do not exceed several volts. Therefore, safety issues are negligible.

3. CDI is suitable for operation in remote areas since it can be operated on solar energy. In this respect, the technology may be considered environmentally clean.

4. As discussed above, energy can be recovered rather simply, namely, by utilizing the electrical energy created by the regenerating unit. This advantage should be viewed in comparison with modern RO energy recovery devices, which are complicated and expensive.

However, there are several clear drawbacks, listed below, that yet limit the process from been used for large-scale installations:

1. Scaling by precipitation of sparingly soluble salts, organic fouling and biofouling are extremely important factors in any water treatment technology. They result in a reduction of water quality, a decline in production rate, and a sharp increase in energy consumption. As already mentioned above, none of the studies on CDI, even those on field case studies, has taken these factors into account to any significant extent. It is well known that high-surface-area carbons, such as active charcoal and carbon aerogels, strongly adsorb organic material, which may constitute nutrients supporting bacterial growth [56]. This problem is also relevant to carbon aerogels, which have become the leading electrode material for CDI. As a result of the promotion of bacterial growth by adsorbed organic material, the CDI electrodes may become covered with a biofilm of bacterial extra-cellular polymers. This biofouling will impede electric charging of the electrodes, followed by loss of ion electrosorption efficiency and increase in energy consumption, as occurs in membrane-based water treatment. To prevent this phenomenon, at least partially, the CDI influent has to be thoroughly pretreated to reduce the concentrations of total organic carbon and scaling factors. This is in contrary to what has been stated elsewhere [55] that "Pretreatment is not a major issue…".

2. As discussed above, electrode material for CDI has been developed to great extent in the last 15 years. However, ways has yet to be found for increasing the practically available surface area for ion electrosorption. This should certainly be done by a careful design of the pore structure of these materials, perhaps by utilizing well defined and highly oriented building elements such as carbon nanotubes [57,58]. Achieving this will not only result in more compact CDI units due to much larger specific adsorption capacity of the electrodes but will also bring about to faster response to changes imposed by the adsorption-regeneration cycles.

3. It should be also emphasized that unlike statements in some publications (e.g., [54,55]) claiming that this technology is suitable for seawater treatment, desalination with CDI is limited to water of low to medium salinity for two reasons: (a) It may be seen from Fig. 8 and the related discussion above that for the salt concentration of seawater (0.6–0.7 M as NaCl) the theoretical differential charge efficiency will decrease by a factor that is more than one order of magnitude larger than that for brackish water; and (b) Fig. 15 shows a comparison of the specific energy consumption for the removal of salt from brackish and seawater by CDI in comparison with the currently available values for RO desali-

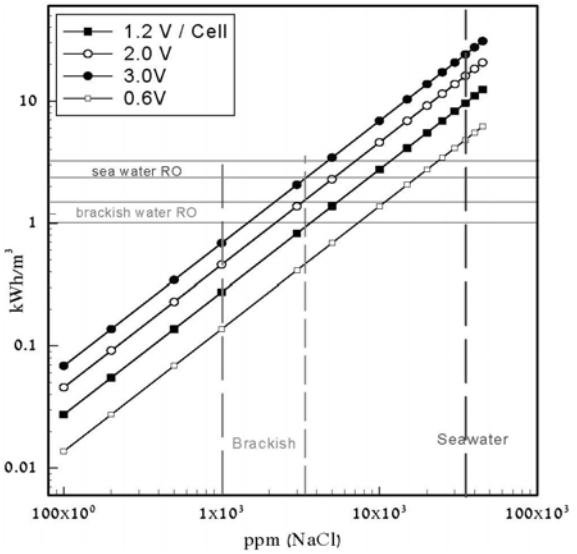

Fig. 15. Specific energy consumption for CDI as a function of NaCl concentration and for different voltages, as compared with brackish and seawater RO desalination.

nation. It is clear that at operative voltages the energy consumption for CDI is much larger than that for seawater RO desalination. However, the values for brackish water desalination by the two technologies are nearly similar. It should be emphasized that energy recovery was not taken into account in Fig. 15. With current technologies, this factor is as high as 30–50% for seawater RO. The experience with energy recovery in CDI is rather limited, and the values provided in the literature are extremely small (6–18%) [52].This point has to be addressed if CDI is to be competitive with other technologies.

In summary, CDI has a long research history, both the pure scientific and the technological aspects, and efforts have also been made towards commercialization. It may be concluded that this technology may be potentially attractive for desalination of low salinity sources such as brackish and surface waters but not for seawater and for removing trace contaminants from polluted streams, as also stated elsewhere [59]. However, it is somewhat disappointing that issues such as scaling and fouling, which constitute major drawbacks for all types of water treatment technologies, have almost not been addressed for CDI. As mentioned above, energy recovery, although a less complex issue for CDI than for other water treatment technologies, should also be studied in depth. Thus, it is apparent that studies of these issues along with improving the electrode material should constitute the future milestones on the road towards a more mature CDI technology.

6. Symbols

A — Factor defined in Eq. (8)
$C_{H\text{-}S}$ — Capacity of diffused double layer, μF cm^{-2}
$C_{M\text{-}H}$ — Capacity of compact double layer, μF cm^{-2}
C_s — Bulk concentration, M
C_T — Total double layer capacity, μF cm^{-2}
E — Electrical potential, Volt
$\mathfrak{F}$ — Faraday number, coulomb equiv^{-1}
g_1,g_2 — Weight of electrodes 1 and 2, g
L — Half the thickness of the electrodes [Eqs. (9), (10)], cm
L_S — Half the thickness of solution layer between electrodes [Eqs. (9), (10)], cm
n_s — Number moles in the solution, mole
Q_d — Normalized q_d [Eq. (8)]
q_d — Two-electrode-cell charge coordinate, coulomb g^{-1}
Q_e — Normalized q_e [Eq. (8)]
q_e — Two-electrode-cell charge coordinate, coulomb g^{-1}
q_1,q_2 — Total charge of electrodes 1 and 2, coulomb
q_1^-, q_1^+, q_2^-, q_2^+ — Anion and cation charge access of electrodes 1 and 2, respectively, coulomb
R — Gas constant, L.atm.mole^{-1} K^{-1}

R_M — Electrode resistance (Fig. 3)
R_S — Solution resistance (Fig. 3)
T — Absolute temperature, K
Vo — Volume of an electrochemical parametric pumping column (Fig. 11), cm^3
ΔV — Volume step of an electrochemical parametric pump (Fig. 11), cm^3
w — Electrical charging work [Eq. (5a)], joule
z — Charge number

Greek

α — Salt diffusivity [Eqs. (9), (10)], $cm^2 s^{-1}$
κ — Specific conductivity of the solution [Eqs. (9), (10)], S cm^{-1}
$\varepsilon, \varepsilon_0$ — Dielectric constant and vacuum permittivity
σ — Specific conductivity of the electrode [Eqs. (9), (10), S cm^{-1}
μ_1, μ_2 — Weight fraction of electrodes 1 and 2
τ_1, τ_2 — Typical time scales [Eqs. (9), (10)], s
φ_H — Potential at plane H at the electrode-solution interface, Volt
Δ — Difference

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