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Capacitive Deionization of NaCl and NaNO₃ Solutions with Carbon Aerogel Electrodes

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ABSTRACT

A process for the capacitive deionization of water with a stack of carbon aerogel electrodes has been developed by Lawrence Livermore National Laboratory. Unlike ion exchange, one of the more conventional deionization processes, no chemicals are required for regeneration of the system. Electricity is used instead. Water with various anions and cations is pumped through the electrochemical cell. After polarization, ions are electrostatically removed from the water and held in the electric double layers formed at the surfaces of electrodes. The water leaving the cell is purified, as desired. The effects of cell voltage and cycling on the electroadsorption capacities for NaCl and NaNO₃ have been investigated and are reported here.

Introduction

A process for the capacitive deionization (CDI) of water with a stack of carbon aerogel electrodes has been developed by Lawrence Livermore National Laboratory. Aqueous solutions of NaCl or NaNO₃ are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m²/g). After polarization, nonreducible and nonoxidizable ions are removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes, as shown in Fig. 1a. As desired, the effluent from the cell is purified water. This process is also capable of simultaneously removing a variety of other impurities. For example, dissolved heavy metals and suspended colloids can be removed by electrodeposition and electrophoresis, respectively. CDI has several potential advantages over other more conventional technologies. Unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the system. Regeneration is accomplished by electrical discharging the cell. Therefore, no secondary waste is generated. In contrast to thermal processes such as evaporation, CDI is much more energy efficient. Since no membranes or high pressure pumps are required, CDI offer operational advantages over electrodialysis and reverse osmosis (RO).

Background

Several publications and patents have appeared that discuss the use of porous electrodes for the recovery of heavy metals from aqueous solutions.¹⁻⁸ In these cases, metallic ions are electrodeposited on the surfaces of cathodes with relatively low specific surface areas. Since deposits can be several atomic layers thick, high specific surface areas are not required. Reticulated vitreous carbon (RVC) foam has been found to be adequate for such applications.

The first studies on CDI appear to have been published at the University of Oklahoma in the early 1960s.^{9,10} The application was desalination of brackish water. A detailed report by Caudle *et al.* describes flow-through capacitors with porous, activated carbon electrodes.¹⁰ Inert polymer-

ic binders were used to hold the carbon particles together in thin conductive sheets. Johnson *et al.* conducted similar studies of reversible electroadsorption, or capacitive deionization, with beds of activated carbon and published their work in the early 1970s.¹¹⁻¹³ Their experimental program included verification of the theoretical basis for process, parametric studies, and evaluation of a variety of candidate electrode materials. Johnson's work prompted Newman to develop a comprehensive theoretical model for the capacitive charging of porous carbon electrodes.¹⁴ Newman's analysis is generally applicable to all CDI systems of this generic geometry. Though CDI was eventually abandoned by Johnson due to various problems, including the failure to demonstrate degradation-free electrode performance, preliminary cost studies did indicate that an efficient, low-cost desalination plant based upon this technology could be built if adequate durability of the electrodes could be achieved. Since this work was conducted decades before the invention of carbon aerogel electrodes, such materials were not included in this study. Several years later, work on CDI was done in Israel and published in the 1980s.¹⁵⁻¹⁷ A column was built from two separated beds of activated carbon, one serving as the anode and the other serving as the cathode. Concentration ratios as high as 1/100 were attained between the top and the bottom of the column. They also developed a theoretical model to predict process performance.

Several practical problems are encountered with conventional activated carbon CDI systems. For example, significant fractions of the carbon surface may be occluded in electrodes that use polymeric binders.^{9,10} Such electrodes have characteristically high electrical and mass-transfer resistances. Furthermore, polymer binders are susceptible to both chemical attack and radiation-induced degradation. Fluorinated polymers are more susceptible to radiation damage than polyethylene and polystyrene. CDI systems that use flow-through beds of activated carbon powder as electrodes require membrane separators for electrical insulation and for preventing entrainment of individual particles in the flow.¹¹⁻¹⁴ Even so, smaller particles generated by erosion of the primary particles can become entrained, thereby depleting the bed. Since raw water flows in the axial direction through the beds, a large

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pressure drop develops. Unfortunately, activated carbon appropriate for use in beds with low pressure drop also has a relatively low specific surface area. Process efficiency is lowered by the large potential drop that develops in thick electrodes and packed beds. Even though adjacent carbon particles may touch, intimate electrical contact may not exist. Consequently, the electrical resistance is high.

Numerous supercapacitors based on various porous carbon electrodes, including carbon aerogel electrodes, have been developed for energy-storage applications.¹⁸⁻²³ However, none of these devices was designed to permit electrolyte flow, and most required membranes to separate the electrodes physically. A double-layer capacitor with a porous activated carbon electrode was developed by Nippon Electric Company of Japan.¹⁸ An electrically conductive layer of activated carbon powder dispersed in butyl rubber, butadiene rubber, polyisoprene, or their copolymers and derivatives was coated onto one side of a current collector. High performance electrodes for double-layer capacitors based on activated carbon fibers were developed by Matsushita Electric Industrial Company.¹⁹ NEC Corporation also developed activated carbon-carbon composite electrodes for a double-layer capacitor.²⁰ Apparently, the first electrodes made of carbonized foamed phenol resin for application in energy storage capacitors were developed by Mitsui Petrochem.²¹ An electrolytic double-layer capacitor for energy-storage-based carbon aerogel, a type of carbon foam, has been developed by Lawrence Livermore National Laboratory.²² The carbon aerogel electrodes used in this device had very high specific surface areas, ranging from 100 to 700 m²/cm² and relatively low corresponding bulk densities, ranging from 0.3 to 1.0 g/cm³. These characteristics made it possible to construct a device with a very high energy density. The electrical continuity of the material permits stored energy to be released rapidly, resulting in a relatively high power density (~7.5 kW/kg). Subsequently, a wide variety of microcellular carbon foams for application in double-layer capacitors was prepared and evaluated by Sandia National Laboratory.²³ These materials were prepared by the controlled pyrolysis and carbonization of several polymers including polyacrylonitrile, polymethacrylonitrile, resorcinol-formaldehyde, divinylbenzene-methacrylonitrile, furfuryl-alcohol, and cellulose polymers such as Rayon. The porosities of these microcellular carbon foams were established by a variety of techniques including gelation, phase separation, emulsion, aerogel-xerogel formation, and replication. Others have also developed composite electrode materials based on activated carbon powder and polymeric binders.²⁴ However, even though these materials are made from activated carbon powders with relatively high specific surface areas (600 m²/g), occlusion limits the useful surface.

The chemistry and physics of small clusters of atoms (1 to 100 nm) has received considerable attention in recent years because these assemblies often have properties between the molecular and bulk solid-state limits.²⁵ The difference observed in properties can be explained in terms of the large fraction of atoms that are at the surface of a cluster as compared to the interior. Although the synthesis and properties of metal and semiconductor clusters, metallocarbohedrenes, fullerenes, and nanotubes are the subject of extensive investigations, little attention has been paid to cluster-assembled porous materials such as carbon aerogels. This oversight is of particular interest to us since we believe that aerogels are one of the few monolithic materials presently available where the benefits of cluster assembly can be demonstrated. In particular, the unique optical, thermal, acoustic, mechanical, and electrical properties of aerogels are directly related to their nanostructure, which is composed of interconnected particles with small interstitial pores. This structure leads to very high specific surface areas (400 to 1100 m²/g) with large fraction of the atoms covering the surface of the interconnected particles. As a result of these structural

features, carbon aerogels have already been used as electrodes in supercapacitors with high energy power densities.²²⁻²⁵ Carbon aerogels provide an almost ideal electrode material because of their low electrical resistivity (≤ 40 m Ω -cm), controllable pore size distribution (≤ 50 nm), and high volumetric surface area (~ 500 m²/cm³). The exceptionally high conductivity of carbon aerogels, in contrast to loosely bonded carbon powders or activated carbon fiber cloths (ACFCs), is attributable to its monolithic structure which is composed of interconnected, covalently bonded carbon particles (~ 12 nm diam). Electrical conduction takes place by both the drift of the delocalized charge carriers within these nanofilaments and the transfer of carriers from one large conducting segment to another by hopping or tunneling. In contrast to electrodes made from compacted carbon powders, the activation energy for transport between carbon particles is relatively small in the carbon aerogels.

This paper discusses the CDI of aqueous solutions with carbon aerogel electrodes. In the application of monolithic carbon aerogel electrodes to CDI, benefits include enhanced electrosorption capacity due to the immense specific surface area and complete immobilization of the porous carbon matrix. Carbon aerogel electrodes can be fabricated that have more accessible surface area than comparable activated carbon powders, thereby enabling greater electrosorption. The exceptional electrical conductivity and thin construction of carbon aerogel electrodes minimize potential drop. Therefore, more ions can be electrosorbed on a unit of carbon aerogel surface area than on a comparable unit of activated carbon surface area. In deep packed beds of carbon, the potential can drop to levels where the electrosorption process is not very effective. Unlike beds of activated carbon powder, monolithic sheets of carbon aerogel are not entrained in the flowing fluid stream. Consequently, the need for porous separators is eliminated. The electrolyte flows in a channel between adjacent anodes and cathodes and does not experience the high pressure drop associated with flow-through packed beds. Since there is no need for polymeric binders, the monolithic carbon aerogel electrodes are relatively resistant to both chemical attack and radiation-induced degradation, provided that polymer-based cements are not used. The economic viability of this CDI process depends upon the life of the carbon aerogel electrodes. To gain insight into electrode life, studies with new, aged, and rejuvenated electrodes are presented.

There are several important potential applications for CDI with carbon aerogel electrodes. Ion exchange is now used as a means for removing anions and cations, including heavy metals and radioisotopes, from process and wastewater in various industries. This process generates large volumes of corrosive secondary wastes during regeneration that must be treated for disposal. After ion exchange columns are saturated, resins must be regenerated by pumping relatively concentrated solutions of acids, bases, or salts through the columns. These solutions become contaminated with ions removed from the resins and become part of a large inventory of secondary waste. Eventually, the resins also become part of the inventory of secondary waste. During plutonium processing, resins and solutions of HNO₃ become contaminated with PuO₂²⁺ and other radioisotopes. In this case, every kilogram of cation exchange resin requires approximately 100 kg of 10 weight percent (w/o) HNO₃ and 2 to 3 kg of rinse water for regeneration. Similarly, every kilogram of used anion exchange resin requires approximately 100 kg of 10 w/o NaOH and 2 to 3 kg of rinse water for regeneration. Given the high and increasing cost of disposal of secondary wastes in mined geological repositories, there is tremendous and still unfulfilled need for reducing, and in certain applications, eliminating the volume of secondary wastes.

CDI could also be used to remove inorganic ions from boiler water for fossil and nuclear power plants. A variety of dissolved inorganic ions have to be removed to prevent scaling of heat exchanger surfaces and to prevent failure

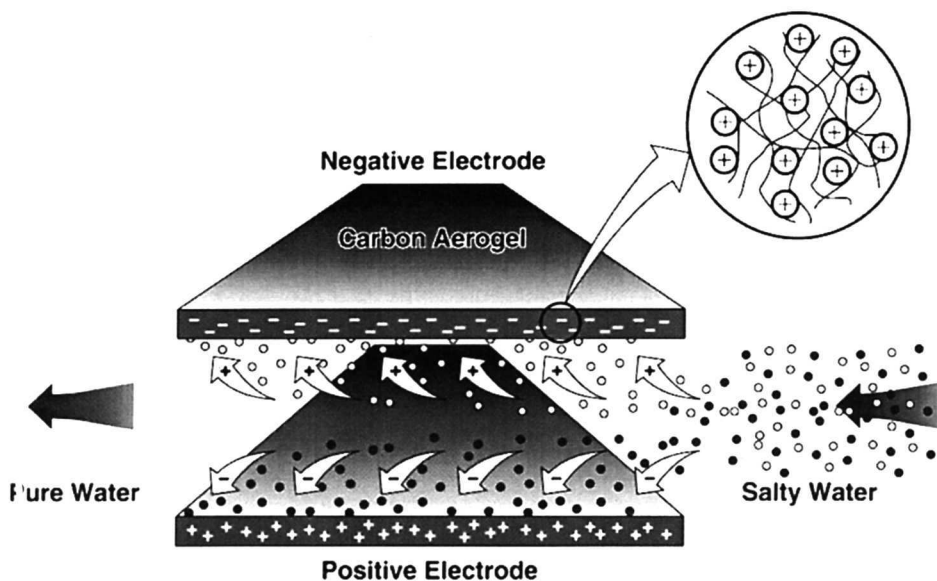
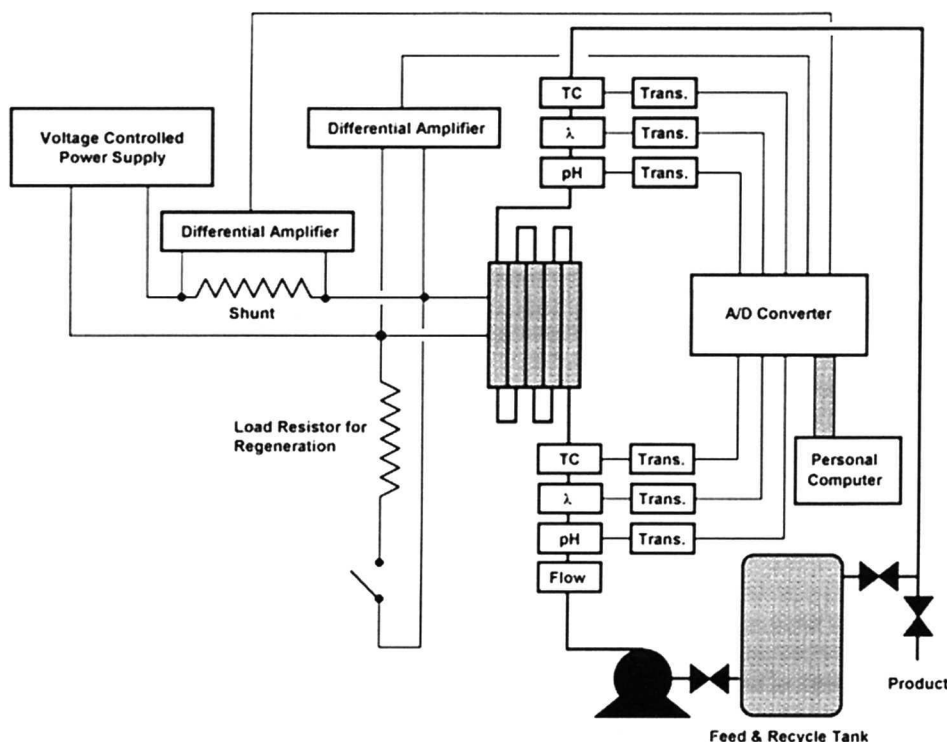


Fig. 1. (a, top) Schematic diagram illustrating the principal of capacitive deionization with carbon aerogel electrodes. Cations and anions are held in the electric double layers formed at the cathode and anode, respectively. The high specific surface area of the carbon aerogel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes. (b, bottom) Schematic diagram showing the apparatus used for demonstration of the capacitive deionization process.



due to pitting and stress corrosion cracking. CDI could also be used to remove radioactive ions from the contaminated wastewater of nuclear power plants before discharge. Deionizers based on columns of zeolite, silica gel, and ion exchange resins were evaluated for the removal of ^{137}Cs , ^{90}Sr , and ^{125}Sb from contaminated water at the Three Mile Island Nuclear Power Station Unit No. 2.²⁶ As previously discussed, ion exchange columns require chemical regeneration and thereby produce large volumes of radioactive secondary waste. Eventually, the contaminated columns also become waste. Since CDI uses electrical regeneration, it seems ideal for such applications.

Experimental

Conceptually, the CDI process is very simple. After application of a voltage between two adjacent carbon aerogel electrodes, cations and anions are drawn toward the cathode and anode, respectively, as illustrated by Fig. 1a. These ions are held in the electric double layers

formed at the extensive surface of the carbon aerogel electrodes until the voltage is reduced. Double-sided electrodes are made by gluing two sheets of a carbon aerogel composite (CAC) to both sides of a titanium plate that serves as both a current collector and a structural support for the CAC. Conductive carbon epoxy is used for gluing. CAC has an exceptionally high specific surface area of 400 to 1100 m^2/g . Each sheet of CAC is $6.86 \times 6.86 \times 0.0127 \text{ cm}$ and has a total active surface of approximately $2.8 \times 10^6 \text{ cm}^2$. Two orifices are located along one side of the carbon aerogel electrode and admit water to the electrode gap. A pattern of holes is located around the perimeter of the titanium plate and accommodates 12 threaded rods that hold the cell stack together. A lower stainless steel header with a rubber gasket and 12 threaded rods; an array of electrodes, gaskets, and spacers; and an upper stainless steel header are assembled into a stack. Even electrodes serve as cathodes while odd electrodes serve as anodes. The electrodes and headers are aligned by the threaded rods. An

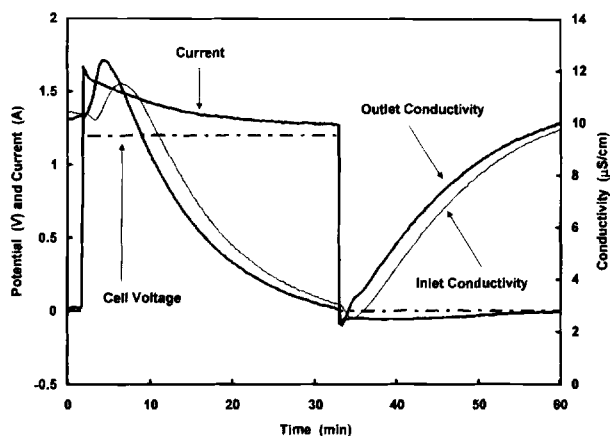


Fig. 2. Deionization of a fixed volume of $10 \mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at a cell voltage of 1.2 V.

electrode separation of 0.05 cm is maintained by cylindrical nylon spacers concentric with the threaded rods and a rubber compression seal. Since the orifices in each electrode alternate from one side of the stack to the other, the flow path through the stack is serpentine. A stack of 192 pairs of carbon aerogel electrodes has a total active surface area of approximately $1.1 \times 10^9 \text{ cm}^2$. Flow through the stack is generated by a programmable, magnetically coupled, screw pump with a 304 stainless steel head. The pressure drop across a stack of 48 electrode pairs is only 35 kPa (5 psi) at 1.7 liter/min, whereas the drop across a stack of 192 electrode pairs is less than 97 kPa (14 psi) at 1.5 liter/min. All lines are made of Teflon and have a nominal diameter of 0.635 cm (1/4 in.). The cells are polarized by programmable power supplies that have a voltage range of 0 to 12 V or a current range of 0 to 60 A. As shown in Fig. 1b, sensors are placed on the inlet and outlet lines of the electrode stack. Electrical conductivity, pH, individual ion concentrations, and temperature are continuously monitored. A computerized data acquisition system logs important operating parameters such as a voltage, current, conductivity, pH, and temperature. The data acquisition system is based on an Intel 486DX-33 microprocessor, a National Instruments eight-channel A/D converter, and LabTech Notebook data acquisition software for Microsoft Windows.

As previously discussed, electrodes are made from thin sheets of CAC glued to titanium plates with conductive

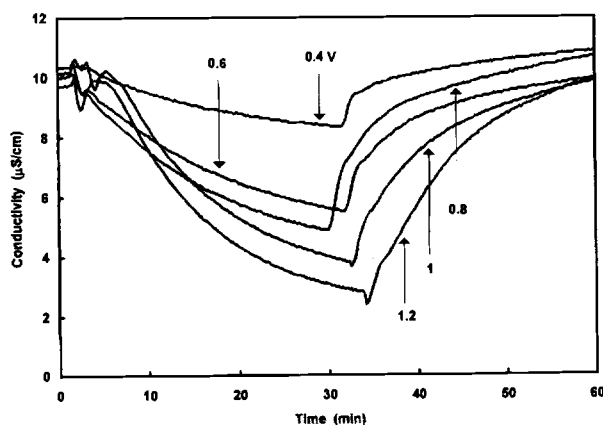


Fig. 3. Deionization of a fixed volume of $10 \mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liter at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at voltage differences ranging from 0.4 to 1.2 V.

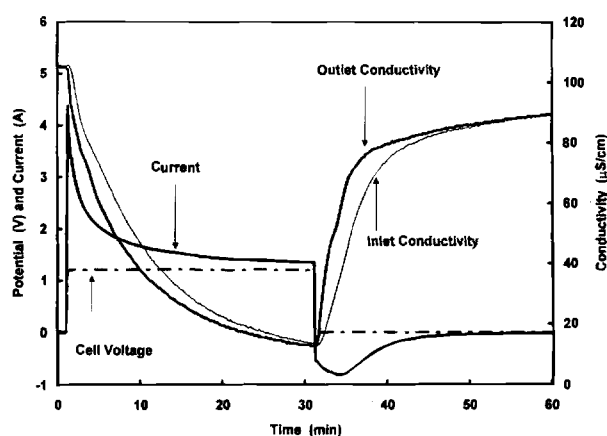


Fig. 4. Deionization of a fixed volume of $100 \mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at a cell voltage of 1.2 V.

epoxy. Carbon aerogels were developed at Lawrence Livermore National Laboratory. The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously.²⁷⁻³⁰ For this study, carbon aerogel composite (CAC) electrodes were formed by infiltrating at 70% w/v RF solution into a porous carbon paper (Lyndall Technical Papers, Rochester, NH). The RF/carbon paper was cured between glass plates in a closed vessel to prevent evaporation. Next, the RF/carbon paper was exchanged into acetone, which was subsequently evaporated at room temperature. It should be noted that these electrodes were not supercritically dried, which is necessary for producing low density organic aerogels. Finally, the RF/carbon paper was pyrolyzed at 1050°C in a nitrogen atmosphere to give thin film electrodes ($\sim 125 \mu\text{m}$ thick) having bulk densities of $\sim 0.6 \text{ g}/\text{cm}^3$. A thin film of graphite-filled epoxy (3:1:3 Epon 828:HY955: graphite) was then applied to the titanium current collectors, and the electrodes were lightly pressed into place. The epoxy was further cured for 24 h at 85°C . This fabrication process results in unique open-cell carbon foams that have high porosities, high specific surface areas (400 to $1100 \text{ m}^2/\text{g}$), ultrafine cell and pore sizes ($\leq 50 \text{ nm}$), and a solid matrix composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of $\sim 12 \text{ nm}$. These quoted specific surface areas are based on Brunauer-Emmett-Teller (BET) analyses. The BET equation is an extension of the Langmuir adsorption

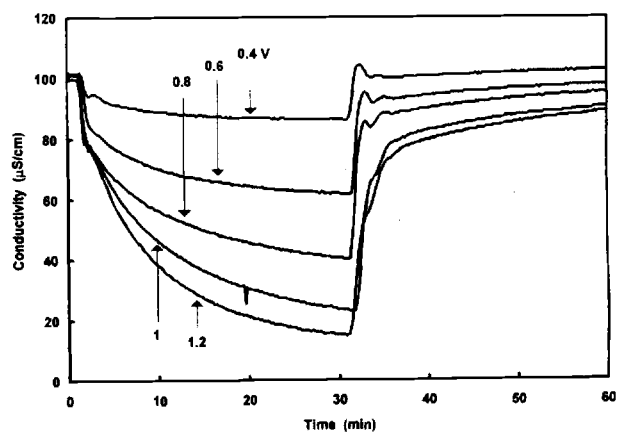


Fig. 5. Deionization of a fixed volume of $100 \mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liter at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at cell voltages ranging from 0.4 to 1.2 V.

isotherm equation and is used for computing the area of an adsorbed monolayer of gas molecules. The monolayer is interpreted as active surface area. The porosity and surface area of aerogels can be controlled over a broad range, while the pore size and particle size can be tailored at the nanometer scale. The three controlling factors are (i) the resorcinol/catalyst (R/C) ratio of the starting solution; (ii) the pyrolysis temperature; and (iii) chemical activation procedures. The R/C ratio affects the number of RF clusters generated in solution and the size to which they grow. For carbon aerogels synthesized at low R/C values, higher surface areas and better particle interconnectivity are achieved. The specific surface area of carbon aerogels is practically independent of the bulk density for the samples prepared at the same R/C ratio. Thus, carbon aerogels with a high bulk density simply have more interconnected particles per unit volume than their low-density counterparts. This feature is critical to achieving high electroadsorption capacity in relatively small volumes.

Initial parametric studies were performed with solutions of NaCl and NaNO₃ in water. In each case, experiments were performed over a broad range of solution conductivity and cell voltage. Conductivities ranged from 10 to 1000 $\mu\text{S}/\text{cm}$, and voltage levels were 0.0, 0.4, 0.6, 0.7, 0.8, 1.0, and 1.2 V. Batch-mode experiments were done by continuously recycling 4.0 liters of electrolyte at a flow rate of 1.0 liter/min. Single-pass experiments were done by pumping 20 liters of electrolyte through the electrode stack at flow rate of 25 ml/min. In this case, there was no recycle.

Results

Overall, tests demonstrated that CDI with carbon aerogel can effectively remove both NaCl and NaNO₃ from water. Deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentration and conductivity of a NaCl solution was cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, *e.g.*, the electroadsorption capacity, had a strong dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.4 V. No severe irreversible degradation in performance was observed after cycling the stacks several months. Breakthrough was observed during single-pass experiments without recycle.

Aged electrodes with 10, 100, and 1000 $\mu\text{S}/\text{cm}$ NaCl solution.—Voltage, current, and solution conductivity data were collected while periodically charging and discharging a stack of 192 pairs of aged carbon aerogel electrodes. Aged electrodes are defined as electrodes that have been cycled semicontinuously for several months. The electrolyte was a solution of NaCl in water and had an initial conductivity of 10, 100, or 1000 $\mu\text{S}/\text{cm}$. Note that NaCl concentration is measured as conductivity and that 1700 $\mu\text{S}/\text{cm}$ corresponds to approximately 1000 ppm. During these batch-mode, fixed-volume experiments with complete recycle, the amplitude of the applied voltage pulse ranged from 0.4 to 1.2 V, the volume of electrolyte was 4.0 liters, and the flow rate through the stack of electrodes was 1.0 liter/min. From the experiment with 10 $\mu\text{S}/\text{cm}$ NaCl solution at 1.2 V and illustrated by Fig. 2, it is clear that the salt concentration drops when the electrodes are polarized. After 32 min of deionization, beginning at 2 min the concentration of the NaCl solution dropped to approximately 3 $\mu\text{S}/\text{cm}$, a reduction of solution conductivity and NaCl concentration of approximately 70%. The salt was placed back into solution by discharging the cell at 32 min. The regeneration was more than 95% complete after 28 min. The process was repeated for numerous cycles without noticeable loss in capacity. The failure of the current to decay asymptotically to zero is believed to have been due to parasitic electrochemical reactions such as oxygen reduction. Unfortunately, the electrolyte in this experiment was not deaerated. Current leakage across the gaskets and spacers was reduced to an insignificant level. Similar experiments were also conducted at cell voltages

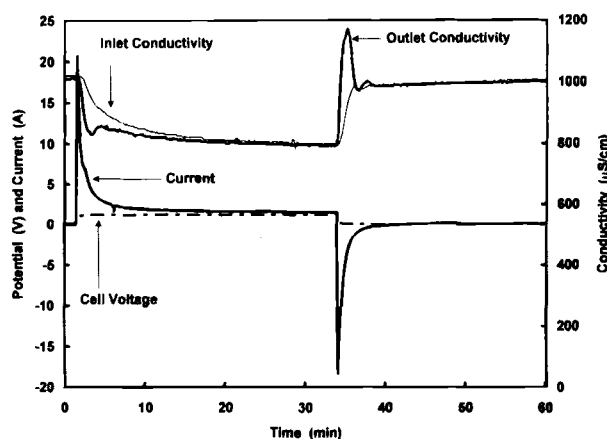


Fig. 6. Deionization of a fixed volume of 1000 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at a cell voltage of 1.2 V.

of 0.4, 0.6, 0.8, and 1.0 V. Transients in solution conductivity for all experiments are shown in Fig. 3. Clearly, more ions are electroadsorbed from solution at higher cell voltages. Experiments were then conducted with a solution of NaCl in water that had an initial conductivity slightly greater than 100 $\mu\text{S}/\text{cm}$. Voltage, current, and solution conductivity transients during one charge-discharge cycle of such an experiment at 1.2 V are shown in Fig. 4. As expected, cations and anions were held in the electric double layers formed at the extensive surfaces of the carbon aerogel cathodes and anodes during charging and released back into the electrolyte during discharge. Consequently, the salt concentration dropped during charging and increased during discharge. The outlet conductivity dropped more quickly than the inlet conductivity during deionization (charging). Similarly, the outlet conductivity increased more quickly than the inlet conductivity during regeneration (discharge). Here too the failure of the current to decay to zero is attributed to parasitic electrochemical reactions or current leakage across gaskets and spacers. Transients in conductivity during batch-mode experiments with 100 $\mu\text{S}/\text{cm}$ NaCl solution at five different applied voltages, 0.4, 0.6, 0.8, 1.0, and 1.2 V, are shown in Fig. 5. The greater the cell voltage, the greater the extent of deionization. The process was very effective at 1.2 V, with much poorer performance at 0.4 V. Electroadsorption capacity decreased as the cell voltage was

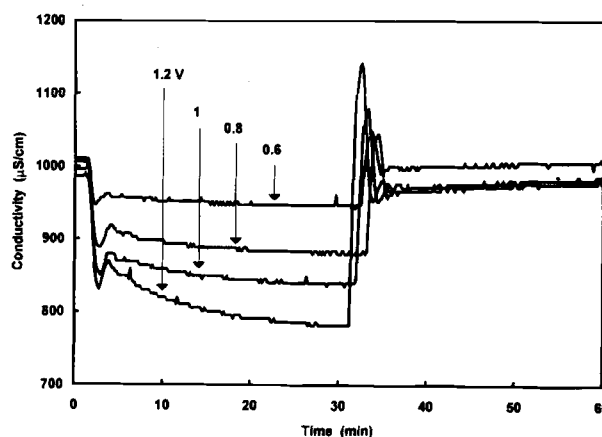


Fig. 7. Deionization of a fixed volume of 1000 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

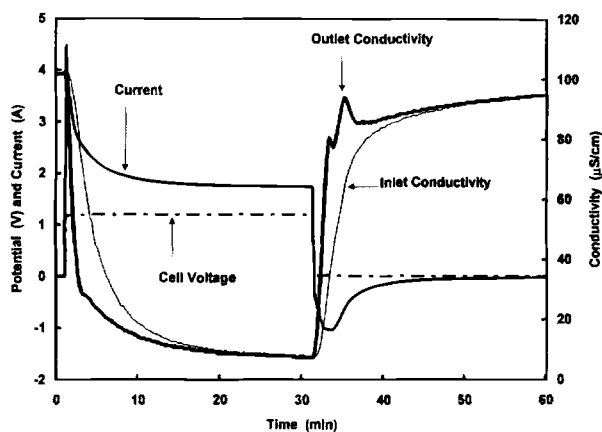


Fig. 8. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 new electrode pairs operated at a cell voltage of 1.2 V.

lowered. Experiments similar to those illustrated by Fig. 4 and 5 in every way except solution conductivity, which was 1000 $\mu\text{S}/\text{cm}$, are illustrated by Fig. 6 and 7. From these data it is concluded that a stack of 192 pairs of aged carbon aerogel electrodes has sufficient electrosorption capacity to remove 20% of the salt from a fixed, 4.0 liter volume of 1000 $\mu\text{S}/\text{cm}$ solution.

New electrodes and 100 $\mu\text{S}/\text{cm}$ NaCl solution.—After experiments with the aged carbon aerogel electrodes were completed, new electrodes were assembled into a stack and tested. The experiments with new electrodes, represented by Fig. 8 and 9, are identical to those with aged electrodes, represented by Fig. 4 and 5, except for the age of the electrodes. The oscillations in the outlet conductivity during discharge are real and are believed to be due to concentration feedback effects. Note that the residence time of the loop is only 4 min, about the same as the period of the oscillation. At a cell voltage of 1.2 V, 192 new pairs of electrodes are capable of removing 93 to 95% of the salt from a fixed, 4.0 liter volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. In contrast, aged electrodes were capable of removing only 85% of the salt. These findings are consistent with those for activated carbon powder obtained by others. The degradation of electrode performance was worse at lower cell voltages. For example, aged electrodes at 0.6 V were capable of removing only 31% of the salt from a fixed, 4.0 liter volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution,

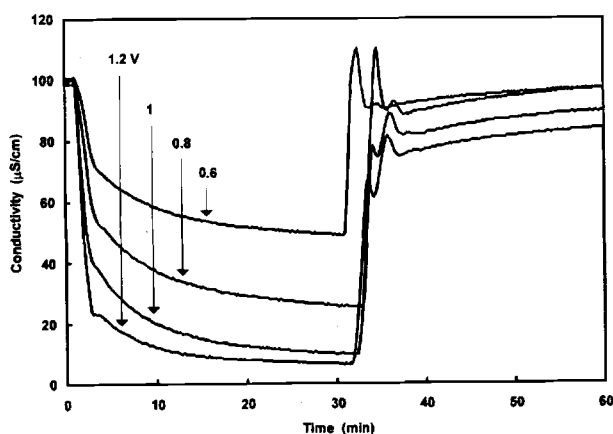


Fig. 9. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 new electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

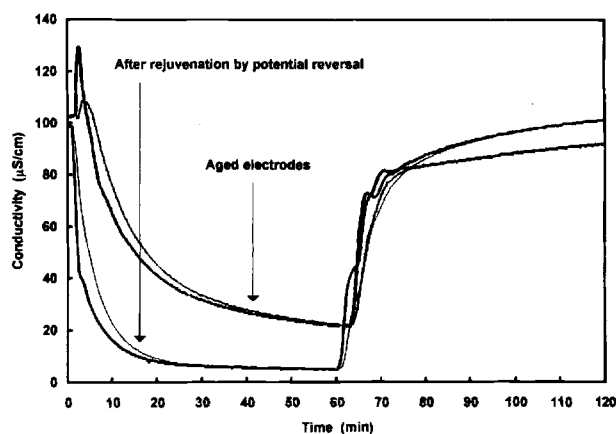


Fig. 10. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 new electrode pairs operated at a cell voltage of 1.2 V.

whereas new electrodes were capable of removing more than 51%.

Rejuvenation of aged electrodes.—Fortunately, as illustrated by Fig. 10, the electrosorption capacity lost with aging can be almost completely recovered by voltage reversal in the cell. Such rejuvenation can be used to increase the electrosorption capacity of aged electrodes back to initial levels. In this case, such operation raised the salt removal from approximately 80% to above 95%. It appears that such rejuvenation can be repeated numerous times with essentially the same desirable result. It is believed that the voltage reversal drives chemically bound ions from the surface of the carbon aerogel by imposing significant repulsive electrostatic force.

Expanded stack and 100 $\mu\text{S}/\text{cm}$ NaCl solution.—After a technique for rejuvenating the electrodes was developed, a stack of 384 pairs of carbon aerogel electrodes was assembled and tested. Half of the electrodes were new and half of the electrodes were aged electrodes that had been rejuvenated by voltage reversal. As shown in Fig. 11, a stack of 384 pairs of carbon aerogel electrodes at 1.2 V removes approximately 97% of the salt in a fixed, 4.0 liter volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. This is only slightly more than that removed with 192 pairs of new or rejuvenated electrodes. In a batch mode with complete recycle, salt

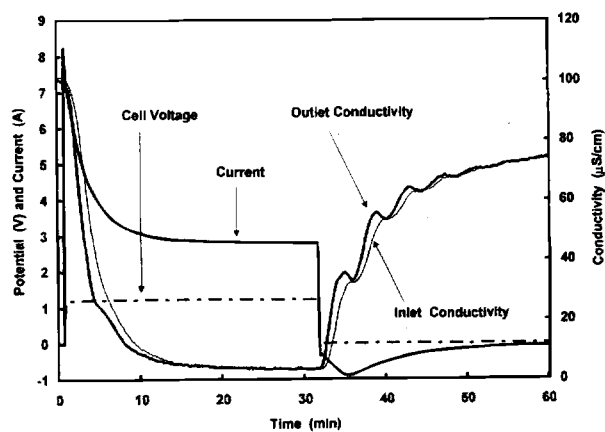


Fig. 11. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 384 electrode pairs (192 aged and 192 new) operated at a cell voltage of 1.2 V.

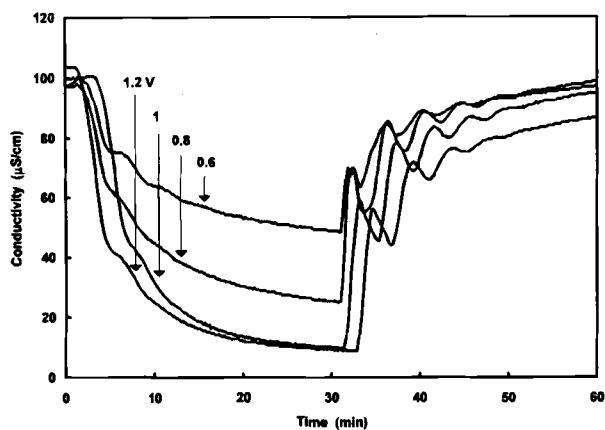


Fig. 12. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 384 electrode pairs (192 aged and 192 new) operated at cell voltages ranging from 0.6 to 1.2 V.

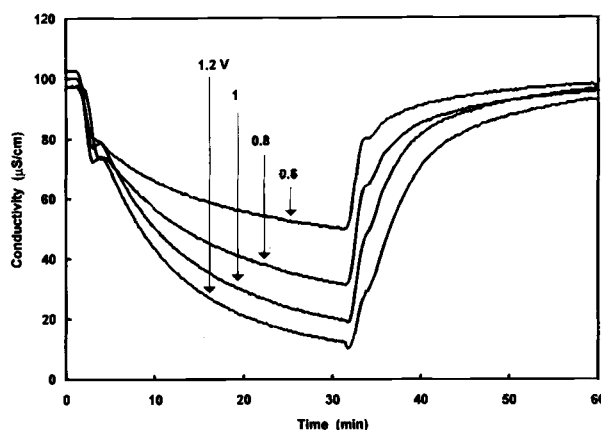


Fig. 14. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

removal does not increase linearly with electrode surface area, as it was expected to. Data for cell voltages of 0.6, 0.8, 1.0, and 1.2 V are compared in Fig. 12. Qualitatively, the results are similar to those for 192 pairs of new or aged CAC electrodes. As the concentration of salt in the electrolyte diminishes, the equilibrium surface charge density decreases, as expected. However, as shown in Fig. 11, salt removal is not a linear function of electrode surface area.

Aged electrodes and 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution.—Experiments were also conducted with a solution of NaNO₃ in water that had an initial conductivity slightly greater than 100 $\mu\text{S}/\text{cm}$. Conditions were identical to those used for the NaCl experiments represented by Fig. 4 and 5. Voltage, current, and solution conductivity transients during one charge-discharge cycle at 1.2 V are shown in Fig. 13. Transients in solution conductivity during batch-mode experiments with four different applied voltages, 0.6, 0.8, 1.0, and 1.2 V are shown in Fig. 14. Qualitatively, the results for NaNO₃ are similar to those for NaCl.

New electrodes and 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution.—The experiments represented by Fig. 15 and 16 are identical to those represented by Fig. 13 and 14 in every respect except the age of the electrodes. At a cell voltage of 1.2 V, 192 new pairs of electrodes are capable of removing 94% of the salt from a fixed 4.0 liter volume of 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution. In contrast, aged electrodes were capable of removing

only 88% of the salt. Here, too, results are qualitatively similar to those obtained with NaCl solutions. The degradation in electrode performance was worse at lower cell voltages. For example, aged electrodes at 0.6 V were capable of removing only 32% of the salt from a fixed, 4.0 liter volume of 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution, whereas new electrodes were capable of removing more than 51%. Electrodesorption capacity was recovered by reversing the cell voltage. Approximately 49% salt removal was achieved after rejuvenation, essentially the same as for new electrodes.

Expanded stack 1000 $\mu\text{S}/\text{cm}$ NaNO₃ solution.—Batch-mode experiments were conducted with a stack having 384 pairs of new and rejuvenated electrodes. As illustrated by Fig. 17, a salt removal of 54% was achieved at 1.2 V, compared to 10% at 0.6 V.

Single-pass experiments with NaCl solutions.—Conductivity transients of NaCl solutions during single-pass experiments with 192 pairs of aged electrodes are shown in Fig. 18 and 19. The amplitude of the applied voltage was 1.2 V, and the flow rate was 25 ml/min. The conductivity dropped to a level below 5 $\mu\text{S}/\text{cm}$ after application of a voltage of 1.2 V across adjacent electrodes, representing a 95% removal of salt from the flowing stream. After 3 to 4 h of operation, the carbon aerogel became saturated (fully charged) with NaCl, and breakthrough was

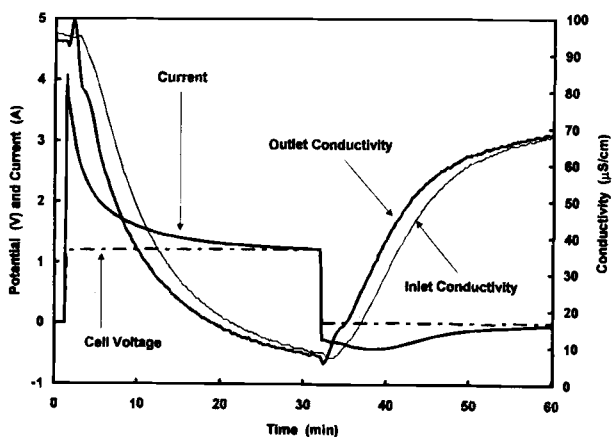


Fig. 13. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 aged electrode pairs operated at a cell voltage of 1.2 V.

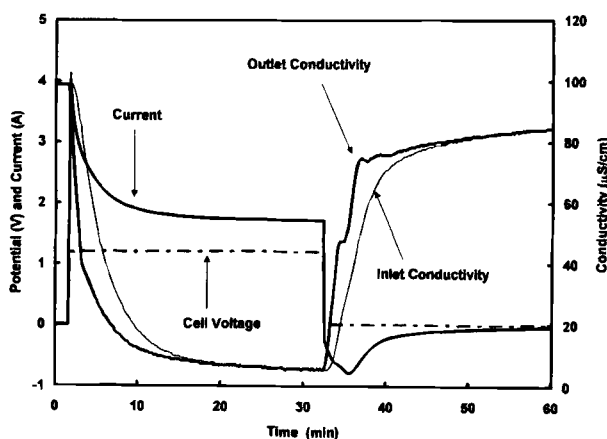


Fig. 15. Deionization of fixed volume of 100 $\mu\text{S}/\text{cm}$ NaNO₃ solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 new electrode pairs operated at a cell voltage of 1.2 V.

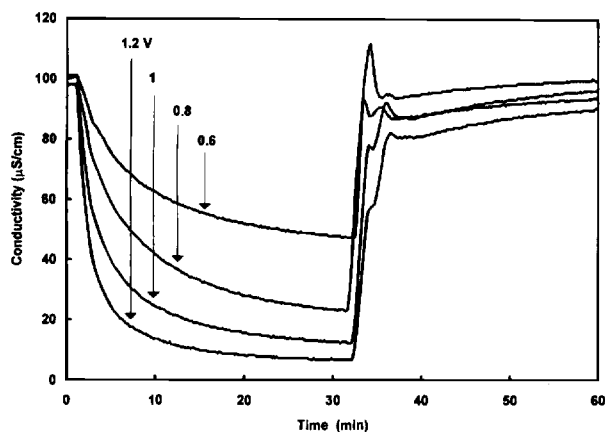


Fig. 16. Deionization of a fixed volume of 100 $\mu\text{S}/\text{cm}$ NaNO_3 solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 192 new electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

observed. The behavior is analogous to that of ion-exchange columns. Conductivity transients during similar single-pass experiment with 1000 $\mu\text{S}/\text{cm}$ NaCl solutions and 384 pairs of new and rejuvenated electrodes are shown in Fig. 20 and 21. There was a significant delay between deionization and regeneration in the experiment illustrated by Fig. 20, which insured complete breakthrough. The operation illustrated by Fig. 21 is similar to that employed for actual purposes of water purification. In both cases, the amplitude of the applied voltage and the flow rate were 1.2 V and 25 ml/min, respectively. The conductivity dropped to a low of 200 $\mu\text{S}/\text{cm}$ after application of a voltage of 1.2 V across adjacent electrodes. The concentration stayed below 400 $\mu\text{S}/\text{cm}$ for 2 h, representing a 60% removal of salt from the flowing stream. After 2 h of operation, the carbon aerogel became saturated (fully charged) with NaCl , and breakthrough was observed.

Summary of results.—The salt removal achieved in experiments at various cell voltages and NaCl concentrations are summarized in Fig. 22. The number of electrode pairs used in these experiments was 192 and adequate for the efficient deionization of 10 to 100 $\mu\text{S}/\text{cm}$ solutions at a cell voltage of 1 to 1.2 V. However, it is clear that higher salt concentrations require more carbon aerogel electrodes for practical levels of desalting. The effect of electrode aging is illustrated by the compilation of data for 100 $\mu\text{S}/\text{cm}$ NaCl and NaNO_3 solutions shown in Fig. 23. In general, electrosorption capacity (salt removal) decreases with cycle life. After several months of operation, the elec-

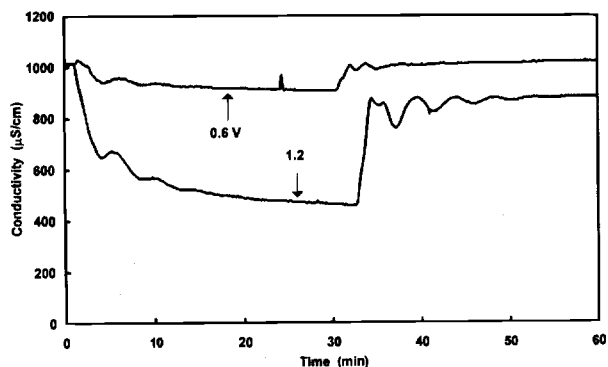


Fig. 17. Deionization of a fixed volume of 1000 $\mu\text{S}/\text{cm}$ NaNO_3 solution. Complete recycle of 4.0 liters at a rate of 1.0 liter/min. The apparatus included 384 electrode pairs (192 aged and 192 new) operated at cell voltage of 0.8 and 1.2 V.

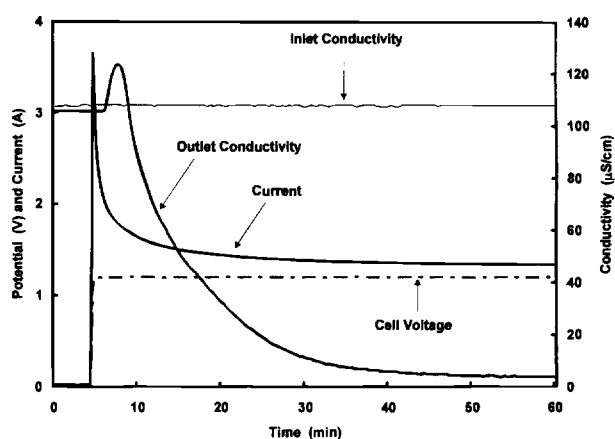


Fig. 18. First hour of a single-pass experiment with 100 $\mu\text{S}/\text{cm}$ NaCl solution at a flow rate of 25 ml/min. The apparatus included 192 aged electrode pairs operated at cell voltage of 1.2 V.

trodes lost 6 to 8% of their capacity of 1.2 V. The effect is more pronounced at lower cell voltages. Fortunately, it appears that most of the loss in capacity can be recovered by periodically reversing the electrode polarization (rejuvenation). Additional aging studies should be performed to quantify electrode life more precisely.

Discussion

From the Gouy-Chapman theory developed for simple planar electrodes, one might expect the surface charge density to have a square root dependence on electrolyte concentration.³¹ For dilute aqueous solutions at 25°C the following expression should be obeyed

$$\sigma = 11.7\sqrt{C} \sinh(19.5 z \phi_0) \quad [1]$$

where σ is the surface charge density ($\mu\text{C}/\text{cm}^2$), C is the electrolyte concentration (mol/liter), z is the ionic charge, and ϕ_0 is the electrode potential (mV). However, in these experiments the average surface charge density appears to be less dependent on concentration

$$\sigma \propto C^{0.1-0.3} \quad [2]$$

It is believed that the observed concentration dependence is due to self-shielding effects experienced by the porous carbon electrode. In most cases, the observed dependence of σ on ϕ_0 is almost linear, as expected.

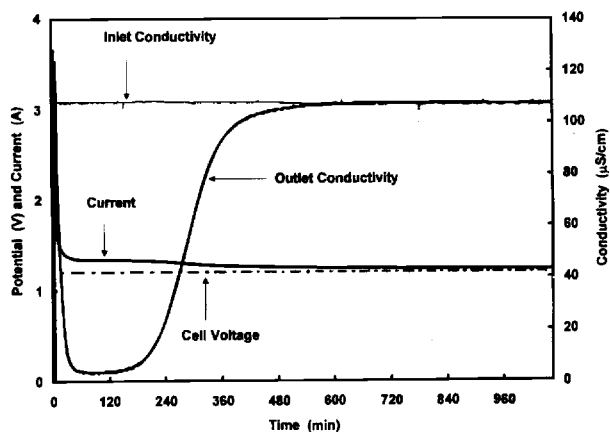


Fig. 19. Entire duration of a single-pass experiment with 100 $\mu\text{S}/\text{cm}$ NaCl solution at a flow rate of 25 ml/min. The apparatus included 192 aged electrode pairs operated at cell voltage of 1.2 V.

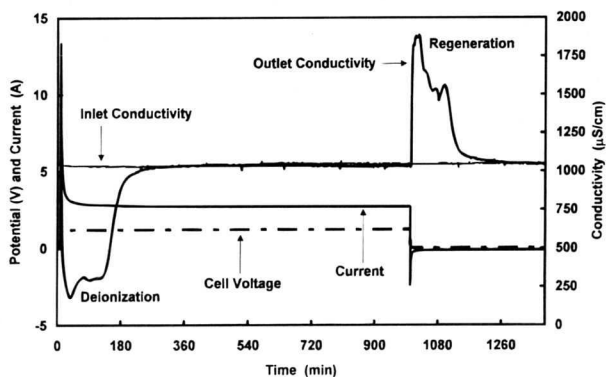


Fig. 20. Entire duration of a single-pass experiment with 1000 $\mu\text{S}/\text{cm}$ NaCl solution at a flow rate was 25 ml/min. The apparatus included 384 electrode pairs (192 aged and 192 new) operated at cell voltage of 1.2 V. Both deionization and regeneration are shown.

The electrosorption capacity of a CDI cell built with porous carbon electrodes is limited by its ability to accommodate anions.¹⁰ Typically, the cation capacity is much higher than the corresponding anion capacity. The mass specific anion capacities for electrodes based on charcoal, carbon black, and graphite are usually below 25×10^{-5} equivalents per gram of carbon at NaCl concentrations of 0.03 N. The anion capacity of carbon aerogel electrodes has been shown to be as good as those made from the best (highest surface area) activated carbons. Table I gives the actual anion capacities while Table II provides values extrapolated to 0.03 N so that they can be compared to published literature values. Extrapolations are based on Eq. 2 and equilibrium electrolyte concentrations reached during polarization. Furthermore, the resistance of a carbon aerogel electrode is much less than a comparable electrode made of activated carbon. For example, the “through resistance” of activated carbon electrodes with polymeric binders is in the range of 1 to 3 Ω ,¹⁰ compared to $\sim 10 \mu\Omega$ for an aerogel electrode.²⁵ The value for the aerogel electrode is based on a measured resistivity of 40 m Ω -cm. Attempts to make direct measurements of the “through resistance” with a standard digital ohmmeter were not possible since the electrode conductivity was so high that it appeared as if the leads were shorted together. Such high conductivity could eliminate the need for expensive metallic substrates. It should be noted that

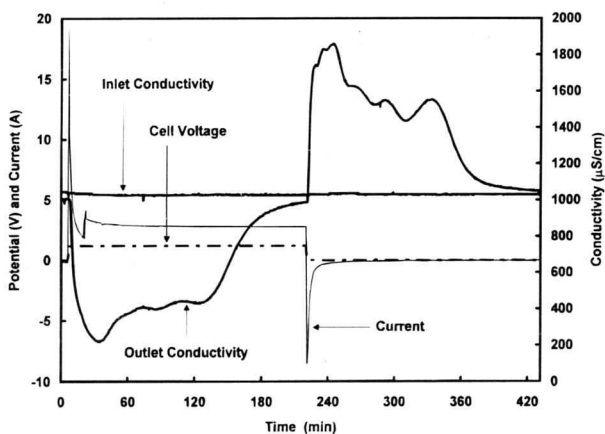


Fig. 21. Entire duration of a single-pass experiment with 1000 $\mu\text{S}/\text{cm}$ NaCl solution at a flow rate was 25 ml/min. The apparatus included 384 electrode pairs (192 aged and 192 new) operated at cell voltage of 1.2 V. Both deionization and regeneration are shown.

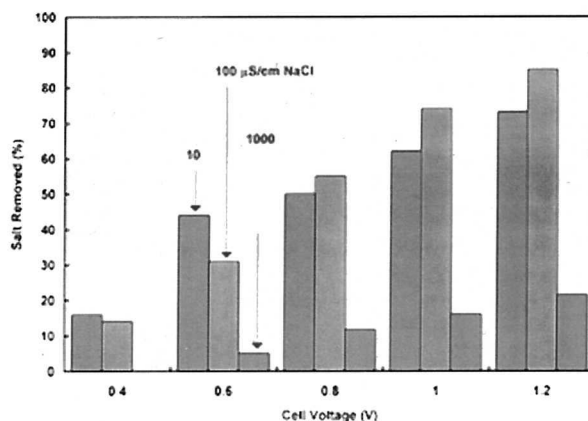


Fig. 22. Salt removal achieved with 10, 100, and 1000 $\mu\text{S}/\text{cm}$ NaCl solutions at cell voltages of 0.4, 0.6, 0.8, 1.0, and 1.2 V. In each case, the electrolyte was a fixed volume of 4.0 liters and the flow rate was 1.0 liter/min. All experiments were conducted with aged electrodes.

the elimination of substrates would also be beneficial in processes designed for radioactive solutions since decontamination would be simplified.

It is noteworthy that activated carbon powders with BET surface areas as high as 3000 m²/g are readily available. However, much of the surface area in such materials is located inside pores having diameters less than 1 nm. It is believed that the electrochemically active area is only a fraction of the BET surface area. BET analyses are probably misleading since gas molecules can penetrate much smaller pores than a typical electrolyte. For example, the bond length of N₂ is only 0.1 nm. It is very doubtful that this level of porosity contributes to electrochemical double layer formation since electrolyte penetration and double layer formation are questionable on this scale. From the Gouy-Chapman theory, as well as the Stern modification of that theory, it is believed that a fully developed electric double layer on a planar electrode with no detrimental shielding effects would require much greater distances for full development.³¹ In the case of a 1:1 electrolyte in water

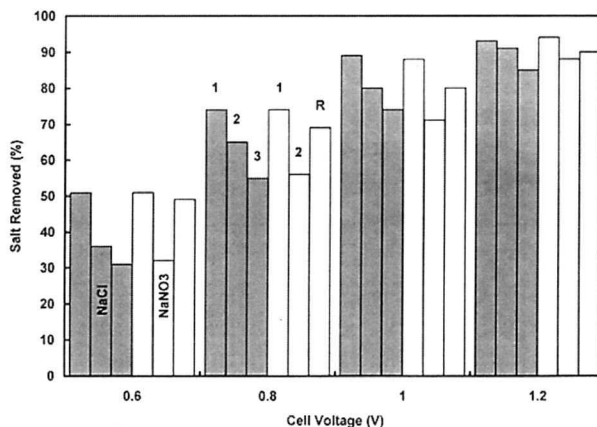


Fig. 23. Data for both NaCl and NaNO₃ solutions showing the effect of aging on the electrosorption capacity of carbon aerogel electrodes. Salt removal at cell voltages ranging from 0.6 to 1.2 V. Complete recycle of a 4.0 liter volume of solution at a rate of 1 liter/min. Data for new electrodes are represented by (1); data for electrodes cycled for several weeks are represented by (2); and data for aged electrodes that have been cycled for several months are represented by (3). Note that (R) represents aged electrodes that have been regenerated by potential reversal.

Table I. Actual anion capacity (equivalents per gram of carbon) $\times 10^5$.

Voltage (V)	10 ppm NaCl New electrode	100 ppm NaCl New electrode	100 ppm NaCl Middle age	100 ppm NaCl Aged electrode	1000 ppm NaCl New electrode
0.6	0.27	3.13	2.21	1.90	5.32
0.8	0.31	4.54	3.98	3.37	12.3
1.0	0.38	5.46	4.90	4.54	16.78
1.2	0.45	5.70	5.58	5.21	22.41

Table II. Anion capacity extrapolated to 0.03 N (equivalents per gram of carbon) $\times 10^5$.

Voltage (V)	10 ppm NaCl New electrode	100 ppm NaCl New electrode	100 ppm NaCl Middle age	100 ppm NaCl Aged electrode	1000 ppm NaCl New electrode
0.6	1.51	9.14	5.96	5.02	6.39
0.8	1.78	16.05	12.89	10.12	15.11
1.0	2.39	24.98	18.77	4.54	20.93
1.2	3.12	29.89	27.13	5.21	28.51

at 25°C, the characteristic thickness of the diffuse layer ranges from 1 nm at a concentration of 10^{-1} M to 20 nm at 10^{-4} M. Finally, published capacitance-density data indicate that the double layer at the carbon-electrolyte interface is primarily formed in the mesopore region.²⁵

If fully developed, CDI with carbon aerogel electrodes could have several important applications. As previously discussed, this technology could be used for the removal of various ions from wastewater without the generation of acid and base secondary wastes. This may be especially important in cases involving radionuclides. At the present time, the United States Department of Energy has an inventory of approximately one billion liters of NaNO₃ solution contaminated with ¹³⁷Cs, ⁹⁰Sr, and other radioactive materials. This technology could also be used for the treatment of boiler water for nuclear and fossil-fired power plants. Such water is now treated with ion exchange to remove ionic contaminants such as Mg²⁺, Ca²⁺, Cu²⁺, and Cl⁻. Elimination of these impurities is essential for the prevention of pitting, stress corrosion cracking, and scaling of heat-transfer surfaces. CDI could be used to replace ion-exchange systems used for the production of high purity water for semiconductor processing. In addition to removing conductivity without the addition of other chemical impurities, the system probably removes small suspended solids by electrophoresis. Furthermore, organic impurities will chemisorb to the carbon. A typical electroplating process involves immersing an object to be electroplated into an electrolyte which contains dissolved metals such as nickel, cadmium, zinc, copper, silver, or gold, as well as variety of salts. After the electroplating process is completed, the plated object is rinsed to remove residual electroplating solution and associated contaminants. Consequently, the rinse water becomes contaminated, creating a major environmental problem for the metal finishing and printed circuit board industry. At the present time, ion exchange is used for the treatment of such rinse water. CDI could provide advantages here as well. It could also be used to soften home drinking water without the introduction of sodium chloride. A typical domestic water softener uses sodium chloride to regenerate a bed of ion exchange resin. Downstream of the ion exchanger, reverse osmosis (RO) is used to remove the sodium chloride introduced during regeneration. A CDI system would not require salt additions for regeneration and would not have to be followed by RO. CDI would also remove heavy metal and organic contaminants from the water. The energy efficiency of such a process and the lack of troublesome membranes could make such a process a contender for desalinating sea water and treating water for irrigation in the Central Valley of California. The minimum theoretical work

required by an isothermal process to separate sea water, which is essentially a 3.5 w/o solution of NaCl in water, into a saturated brine solution and a stream of 10 ppm drinking water is calculated to be approximately 67 J/mol (4.2 Wh/gal) by the authors, assuming that the NaCl obeys the Debye-Hückel activity-coefficient model.^{32,33} The energy required by CDI is of the order $QV/2$ where Q is the stored electrical charge and V is the voltage between adjacent electrodes, and is approximately eight times the theoretical minimum. However, if any of the stored electrical energy is reclaimed during regeneration, or electrical discharge, the energy requirement could be reduced to a level well below this provided that voltage conversion devices are employed. Of course, parasitic electrochemical charge-transfer reactions, leakage currents, and ohmic losses will lower the energy efficiency, probably by 20 to 30%. Such low energy requirements make this process more attractive than thermal processes and extremely competitive with the best known RO systems with energy-recovery turbines. More precise energy analyses are warranted.

Future Work

Parasitic reactions such as oxygen reduction should be minimized to the extent possible since such processes would reduce capacitance and electrosorption capacity by ion displacement and depolarization. Parametric studies should be performed with other salts, as well as acidic and basic electrolytes. Higher concentrations should be explored. A fully automated CDI system that consists of two stacks of aerogel electrodes in parallel has been built and tested. This system enables one stack to be regenerated (discharged) while the other deionizes (charges). This mode of operation is known as potential-swing electrosorption and is analogous to pressure-swing gas absorption. During potential-swing operation, a portion of the current produced during regeneration could be used for purification so that the overall energy efficiency of the process is improved. Chromatographic separation of ions should also be attempted. Theoretically, the system should have ionic selectivity, depending upon the size, charge, and complexation of the ions being separated. This is supported by the observed difference in breakthrough times for NaCl and NaNO₃. Though Cl⁻ and NO₃⁻ anions have the same charge, they have different sizes and degrees of complexation. These initial parametric studies have not provided sufficient data for conclusive statements about the performance of the electrodes over extended periods of time (years). Aging tests should be performed to determine the effects of voltage cycling on electrosorption capacity. Ultimately, the number of electrodes should be increased so that the continuous desalination of seawater

can be demonstrated. More precise energy analyses should be performed. In such applications, this technology may have the potential to enhance the general standard of living in areas with limited water of poor quality.

Conclusions

The capacitive deionization (CDI) of aqueous solutions of NaCl and NaNO₃ with carbon aerogel electrodes has been demonstrated for the first time. Cell voltages ranging from 0 to 1.2 V were investigated. The best performance (salt removal) was achieved at 1.2 V. In experiments without recycle, 95% of the salt in a 100 μS/cm feed stream was removed until saturation of the carbon aerogel electrodes was reached. The number of electrode pairs used in these experiments was 192 and adequate for the efficient deionization of 10 to 100 μS/cm solutions at a cell voltage of 1 to 1.2 V. However, it is clear that higher salt concentrations require more carbon aerogel electrodes for practical levels of desalting. In general, electrosorption capacity (salt removal) decreases with cycle life. After months of operation, the electrodes lost 6 to 8% of their capacity at 1.2 V. The effect is more pronounced at lower cell voltages. Fortunately, it appears that most of the loss in capacity can be recovered by periodically reversing the electrode polarization (rejuvenation). Additional aging studies should be performed to quantify electrode life more precisely. Carbon aerogel CDI offers several potential advantages over conventional thermal and membrane processes for water treatment and deserves further investigation.

Acknowledgments

Funding for this project was provided by the Strategic Environmental Research and Development (SERDP) Program. This work was done under the auspices of the U.S. Department of Energy (DOE) by Lawrence Livermore National Laboratory (LLNL) under Contract No. W-7405-Eng-48.

Manuscript submitted May 31, 1995; revised manuscript received Aug. 18, 1995.

Lawrence Livermore National Laboratory assisted in meeting the publication costs of this article.

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