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Capacitive Deionization of Seawater

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ABSTRACT

Capacitive deionization with carbon aerogel electrodes is an efficient and economical new process for removing salt and impurities from water. Carbon aerogel is a material that enables the successful purification of water because of its high surface area, optimum pore size, and low electrical resistivity. The electrodes are maintained at a potential difference of about one volt; ions are removed from the water by the imposed electrostatic field and retained on the electrode surface until the polarity is reversed. The capacitive deionization of water with a stack of carbon aerogel electrodes has been successfully demonstrated. The overall process offers advantages when compared to conventional water-purification methods, requiring neither pumps, membranes, distillation columns, nor thermal heaters. Consequently, the overall process is both robust and energy efficient. The current state of technology development, commercialization, and potential applications of this process are reviewed.

INTRODUCTION

Technologies for the desalination of seawater to produce potable water for domestic and agricultural use has been extensively reviewed [1, 2]. Principle approaches have been to separate either water from the solution (e.g., thermal distillation, reverse osmosis) or ions from the water (e.g., electrodialysis, ion exchange). The high salt content ($\approx 3.5\%$) plus varying solid particulate levels in seawater provide a continuing challenge to all separation processes from the standpoint of cost and efficiency. Frequently a separation technique has to used in conjunction with other techniques, and improvements in materials or energy sources enables the development of new technical solutions which then have to be evaluated on the basis of cost and efficiency. The development of aerogels has recently provided such an enabling impetus, resulting in new developments in the basic technology of capacitive deionization.

Capacitive deionization (CDI) involves the use of porous electrodes to remove dissolved ions through application of an electrostatic field. A process for the capacitive deionization of water with a stack of carbon aerogel electrodes has been developed at Lawrence Livermore National Laboratory. Aqueous solutions of NaCl or $NaNO_3$ are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m^2/g). After polarization, non-reducible and non-oxidizable 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 Figure 1. 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 electrically 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 offers 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 [3-7]. In these cases, metallic ions are electrodeposited on the surfaces of cathodes with relatively low specific surface areas.

The first studies on CDI appeared in the early 1960s describing flow-through capacitors with porous, activated-carbon electrodes for the desalination of brackish water [8]. Similar studies of reversible electrosorption, or capacitive deionization, with beds of activated carbon were done in the early 1970s [9]. Subsequent work led to the development of a comprehensive theoretical model for the capacitive charging of porous carbon electrodes [10]. Several years later, work on CDI was done in Israel and

published in the 1980's [11]. Though CDI was eventually abandoned for water treatment 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 [10]. Since this work was conducted decades before the invention of carbon aerogel electrodes, such materials were not included in the study.

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 [8]. Such electrodes have characteristically high electrical and mass transfer resistances. Furthermore, polymer binders are susceptible to both chemical attack and radiation-induced degradation. CDI systems that use flow-through beds of activated carbon powder as electrodes require membrane separators for electrical insulation and to prevent entrainment of individual particles in the flow [9,10]. Even so, smaller particles generated by erosion of the primary particles can become entrained, thereby depleting the bed. Since raw water is flown in the axial direction through the beds, a large 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 [12]. However, none of these devices were designed to permit electrolyte flow and most required membranes to physically separate the electrodes. Double-layer capacitors with porous activated carbon electrodes were developed in Japan using various carbon materials (e.g., carbon powders [12]). An electrolytic double-layer capacitor for energy storage based on carbon aerogel has been developed by Lawrence Livermore National Laboratory [13]. The carbon aerogel electrodes used in this device had very high volumetric surface areas, ranging from 100 to 700 m^2/cm^3 and relatively low corresponding bulk densities, ranging from 0.3 to 1.0 g/cm^3. 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 (>2 kW/kg).

This paper discusses the CDI of aqueous solutions with carbon aerogel electrodes. The economic viability of this 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 besides desalination. Ion exchange is now used as a means for removing anions and cations, including heavy metals and radioisotopes, from process and waste water in various industries. This process generates large volumes of corrosive secondary wastes that must be treated for disposal through regeneration processes. CDI could also be used to remove inorganic ions from boiler water for fossil and nuclear power plants.

EXPERIMENTAL
System assembly

Conceptually, the CDI process is very simple. After application of a voltage between two adjacent carbon aerogel electrodes, cations and anions are drawn towards the cathode and anode, respectively, as illustrated in Figure 1. 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. CAC has an exceptionally high specific surface area of ~500 m^2/g. Two orifices are located along one side of the carbon aerogel electrode and admit water to the electrode gap. A lower stainless steel header with a rubber gasket and 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. An 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 10^9 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 0.35 kg/cm^2 (5 psi) at 1.7 L/min, whereas the drop across a stack of 192 electrode pairs is less than 0.98 kg/cm^2 (14 psi) at 1.5 L/min. Electrical conductivity, pH, individual ion concentrations, and temperature are continuously monitored. A computerized data acquisition system logs important operating parameters such as voltage, current, conductivity, pH, and temperature.

Aerogels

As previously discussed, electrodes are made from thin sheets of CAC glued to titanium plates with a conductive, graphite-filled epoxy. The development of aerogels serve as the enabling technology which makes this CDI system technically and economically attractive. The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [14-16]. For this study, carbon aerogel composite (CAC) electrodes were formed by infiltrating a 70 % w/v RF solution into a porous carbon paper (Lydall 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 (~125 μm thick) having bulk densities of ~0.6 g/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 hours at 85°C.

Initial solutions

Initial parametric studies were performed with solutions of NaCl and NaNO$_3$ in water. In each case, experiments were performed over a broad range of solution conductivity and cell voltage. Conductivities ranged from 10 to 1000 μmS/cm (mmho/cm, where 1700 μS/cm corresponds to approximately 1000 ppm of NaCl) 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 L of electrolyte at a flow rate of 1.0 L/min. Single-pass experiments were done by pumping 20 L of electrolyte through the electrode stack at flow rate of 25 ml/min (in the single-pass case, there was no recycle).

RESULTS

Overall, tests demonstrated that CDI with carbon aerogel can effectively remove both NaCl and NaNO$_3$ 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, i.e., the electrosorption 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. Rejuvenation of aged electrodes can be almost completely recovered repeatedly by voltage reversal.

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 semi-continuously for several months. The electrolyte was a solution of NaCl in water and had an initial conductivity of 10, 100, or 1000 μS/cm. During these batch-mode, fixed-volume experiments with complete recycle, the volume of electrolyte was 4.0 L, and the flow rate through the stack of electrodes was 1.0 L/min. Representative data are shown in Figure 2 for 100 μS/cm NaCl solution at 1.2 V, illustrating the drop in salt concentration when the electrodes are polarized. 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 failure of the current to decay to zero is attributed to parasitic electrochemical reactions or current leakage across gaskets and spacer. The removal process was very effective at 1.2 V, with much poorer performance at 0.4 V. Similar data were obtained at 10 and 1000 μS/cm NaCl solutions. 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 L volume of 1000 μS/cm solution, and 70% at an initial concentration of 10 μS/cm, with greater than 95% regeneration. Slightly better results were obtained with new electrodes, although there were transient oscillations in the outlet conductivity during discharge; these are believed to be related to concentration feedback effects.

Fortunately, as illustrated by Figure 3, 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 a significant repulsive electrostatic force.

Representative conductivity transients for NaCl solutions during single-pass experiments with 384

electrode pairs (half new, half rejuvenated) are illustrated in Figure 4. The amplitude of the applied voltage was 1.2 V and the flow rate was 25 ml/min. The operation illustrated by Figure 4 is similar to that employed for actual purposes of water purification. The conductivity dropped to a low of 200 μS/cm after application of a voltage of 1.2 V across adjacent electrodes. The concentration stayed below 400 μS/cm for 2 hours, representing a 60% removal of salt from the flowing stream. After 3 total hours of operation, the carbon aerogel became saturated (fully charged) with NaCl and breakthrough was observed. At an initial concentration of 100 μS/cm NaCl, conductivity dropped to a level below 5 μS/cm after application of a voltage of 1.2 V across adjacent electrodes, representing a 95% removal of salt from the flowing stream.

Similar results were obtained with $NaNO_3$. Figure 5 summarizes salt removal achieved in experiments at various cell voltages and NaCl concentrations. 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. The effect of electrode aging is illustrated by the compilation of data for 100 μS/cm NaCl and $NaNO_3$ solutions shown in Figure 6. In general, electrosorption capacity (salt removal) decreases with cycle life. After several 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.

DISCUSSION

From the Gouy-Chapman theory developed for simple planar electrodes, the surface charge density is expected to have a square root dependence on electrolyte concentration. However, in these experiments the average surface charge density appears to be less dependent on concentration, presumably due to self-shielding effects experienced by the porous carbon electrode. In most cases, the observed dependence of surface charge density on electrode potential is almost linear, as expected.

The electrosorption capacity of a CDI cell built with porous carbon electrodes is limited by its ability to accommodate anions. Typically, the cation capacity is much higher than the corresponding anion capacity. 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. Furthermore, the electrical resistance of a carbon aerogel electrode is much lower than a comparable electrode made of activated carbon. Finally, although other carbon materials may have higher BET surface areas, those materials have much of the surface area located inside pores having diameters less than 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; thus, the electrochemically active area is only a fraction of the measured BET surface area.

In the application of carbon aerogel electrodes to CDI, benefits include enhanced electrosorption capacity due to the high volumetric 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 high electrical conductivity and thin construction of carbon aerogel electrodes minimize potential drop. Thus, more ions can be electrosorbed on a unit of carbon aerogel surface area than on a comparable unit of activated carbon surface area. 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 carbon aerogel electrodes are relatively resistant to both chemical attack and radiation-induced degradation.

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 waste water without the generation of acid and base secondary wastes. This may be especially important in cases involving radionuclides. 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 Mg^{+2}, Ca^{+2}, Cu^{+2}, 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 ions without the addition of other chemical impurities, the system probably removes small suspended solids by electrophoresis. Furthermore, organic impurities will chemisorb to the carbon. 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 weight percent solution of NaCl in water, into a saturated brine solution and a stream of 10 ppm drinking water is calculated to be approximately 16 cal/mol (4.2 Wh/gal). 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 (8X) 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 20-30%. 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 hence electrosorption capacity. Additional studies should be performed with other salts and higher concentrations. 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 while the other deionizes (i.e., potential-swing electrosorption). 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. These initial parametric studies have not provided sufficient data for conclusive statements about the performance of the electrodes over extended periods of time (years). Ultimately, the number of electrodes should be increased so that the continuous desalination of sea water can be demonstrated. More precise energy analyses should also 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 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. Higher salt concentrations will require more carbon aerogel electrodes for practical levels of desalting. In general, electrosorption capacity (salt removal) decreases with cycle life (e.g., 6-8% after several months). Fortunately, it appears that most of the loss in capacity can be recovered by periodically reversing the electrode polarization (rejuvenation). Additional aging studies are being 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

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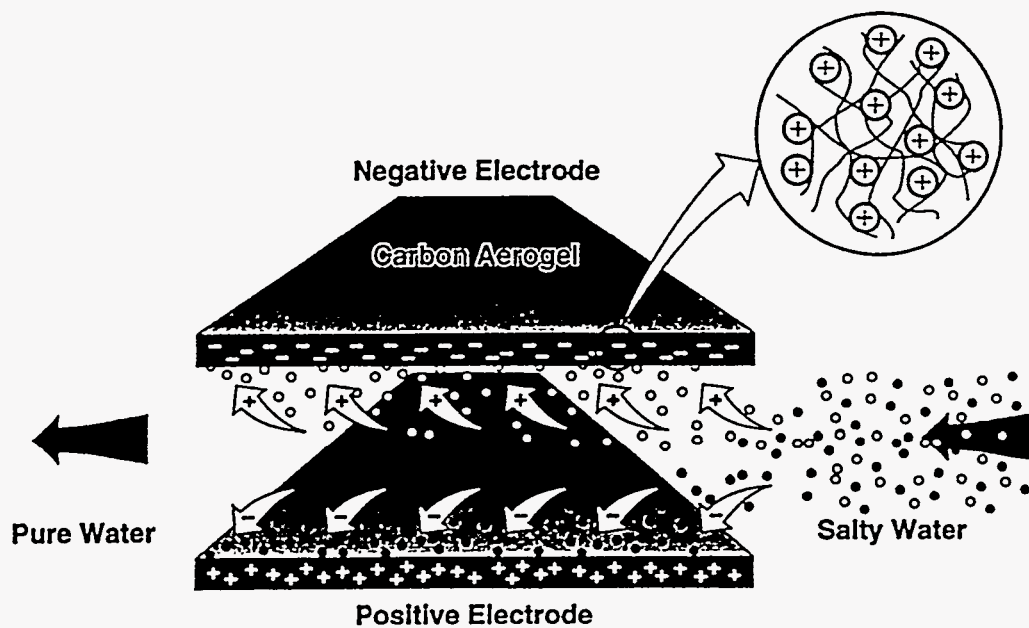
Figure 1. Schematic diagram illustrating the principal of capacitive deionization with carbon aerogel electrodes. Cations and anions are held in the electric double layers formed at the cathode and anode, respectively. The high specific surface area of the carbon aerogel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes.
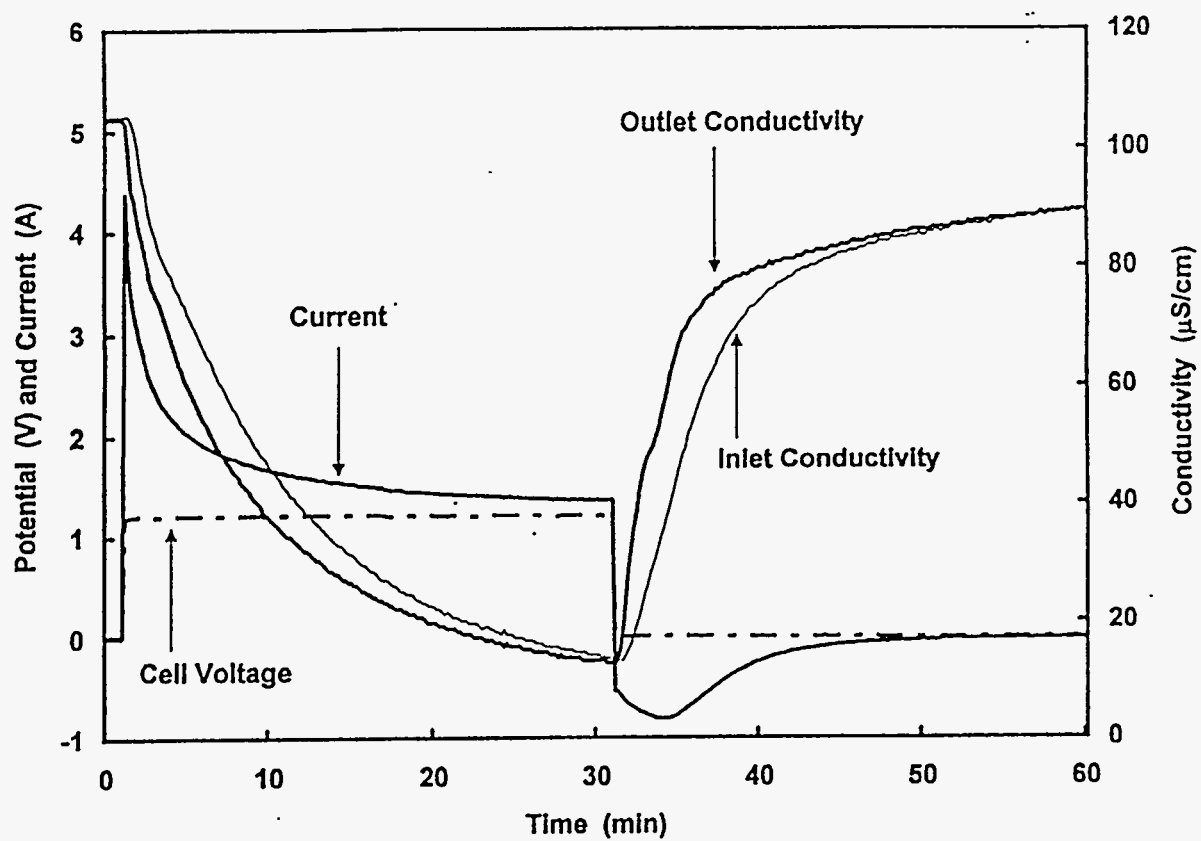
Figure 2. Deionization of a fixed volume of 100 μS/cm NaCl solution. Complete recycle of 4.0 L at a rate of 1.0 L/min. The apparatus included 192 aged electrode pairs operated at a cell voltage of 1.2 V.
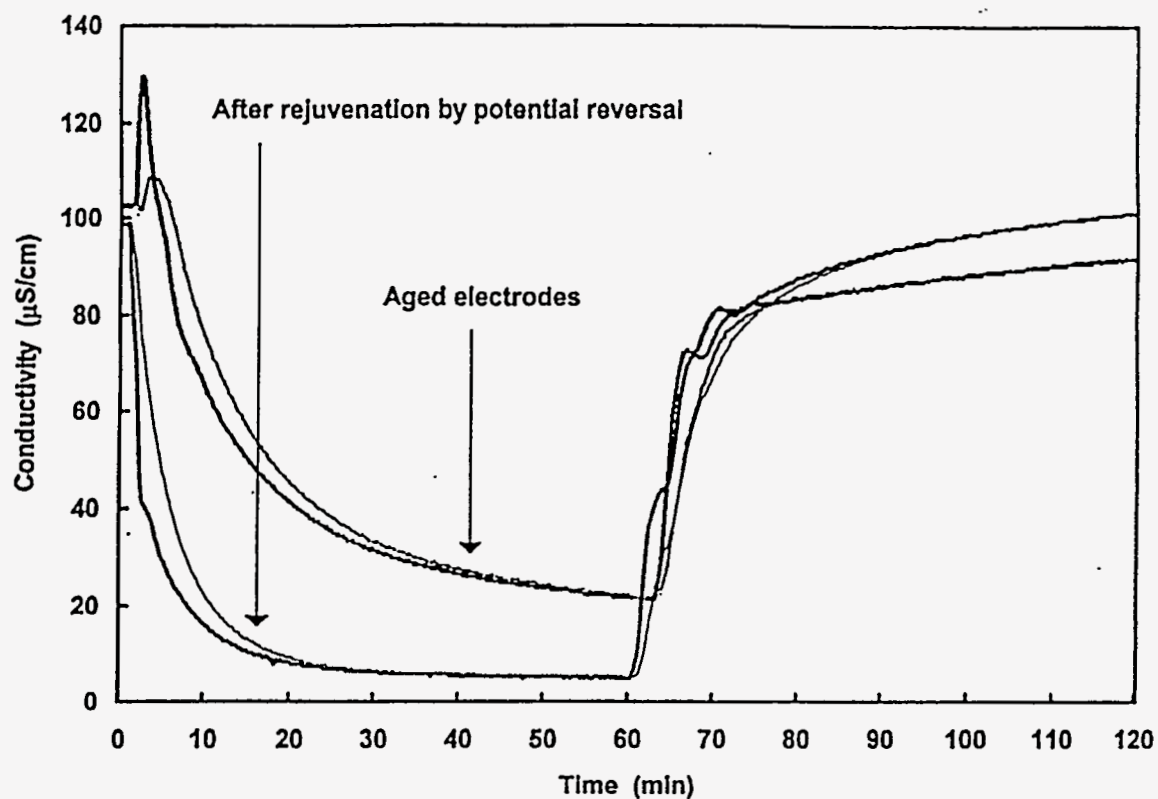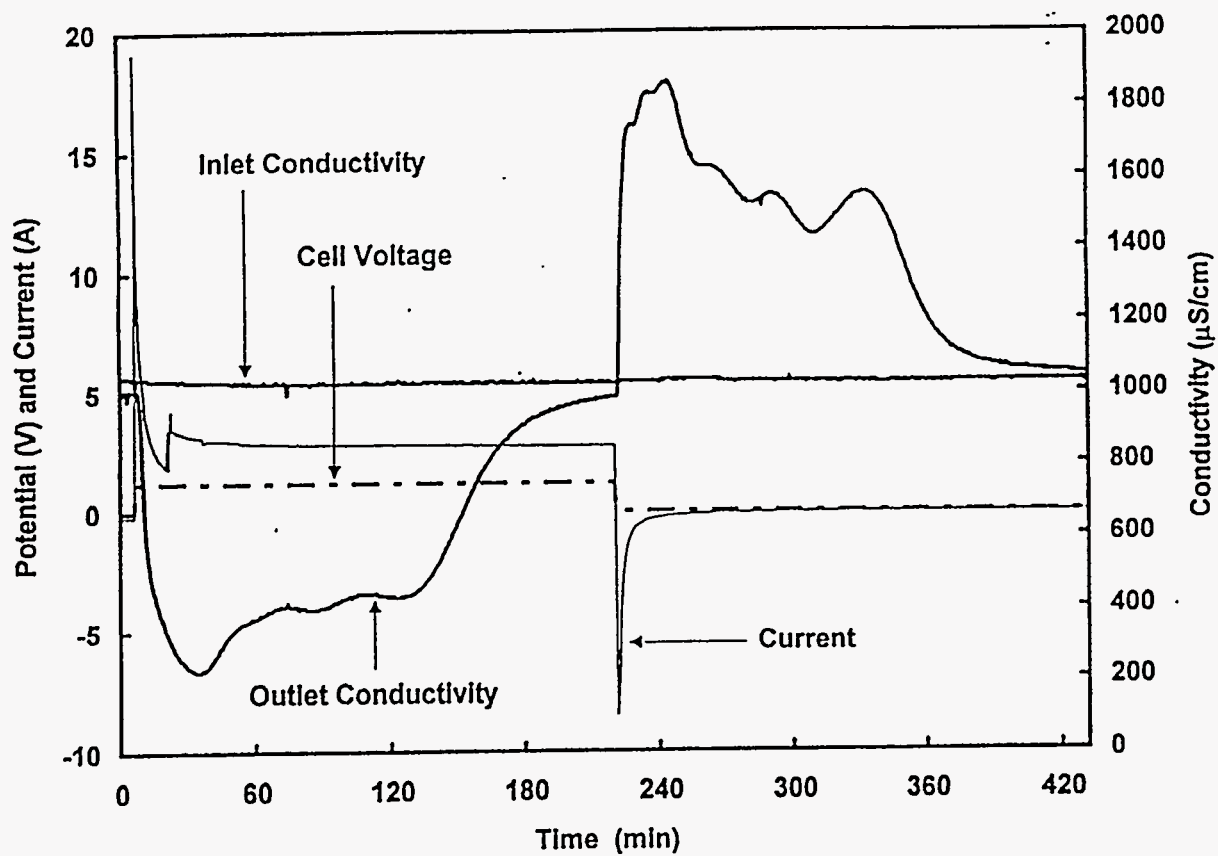
Figure 3. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 µS/cm NaCl solution. Complete recycle of 4.0 L at a rate of 1.0 L/min. The apparatus included 192 new electrode pairs operated at a cell voltage of 1.2 V.

Figure 4. Entire duration of a single-pass experiment with 1000 µS/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.
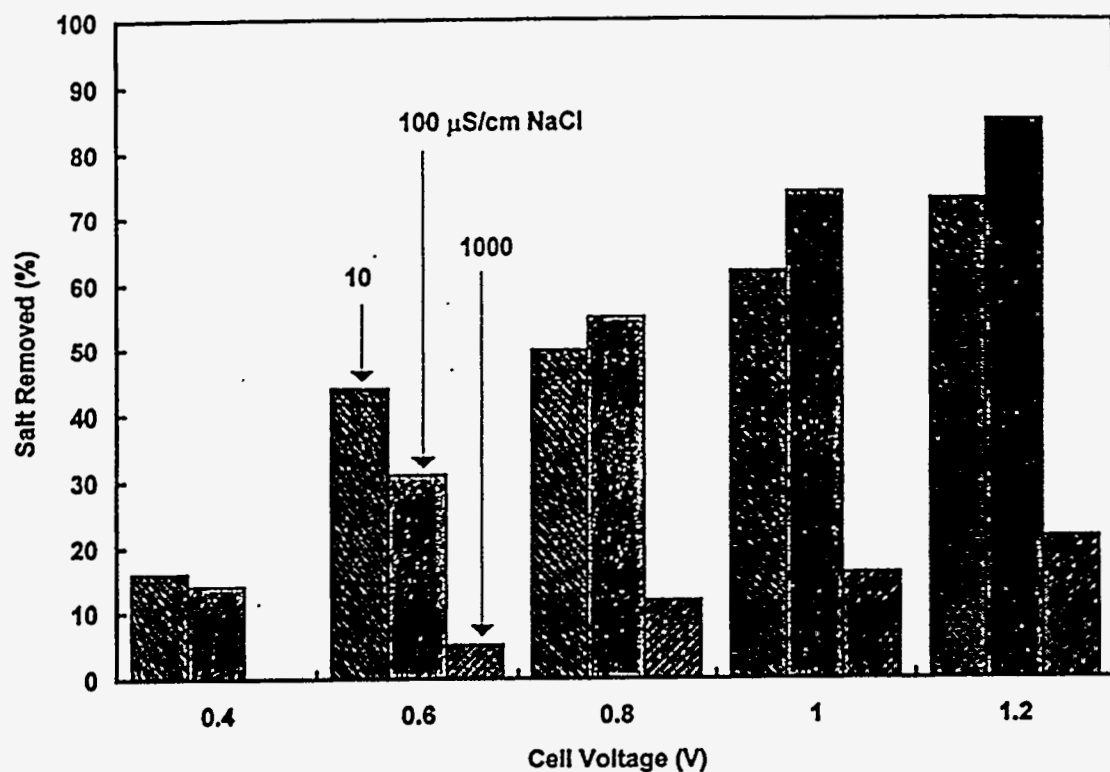
Figure 5. Salt removal achieved with 10, 100, and 1000 µS/cm NaCl solutions at cell voltages of 0.4, 0.6, 0.8, 1.0, and 1.2 V. In each case, the electrolyte was a fixed volume of 4.0 L and the flow rate was 1.0 L/min. All experiments were conducted with aged electrodes.
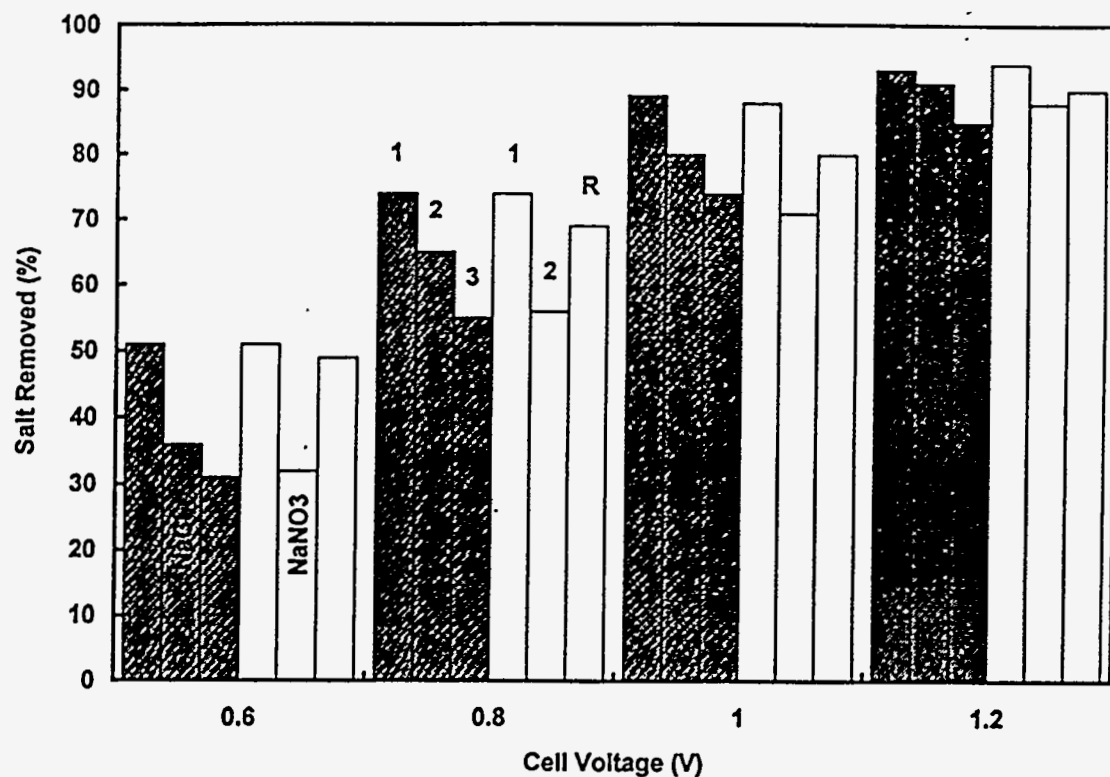
Figure 6. Data for both NaCl and NaNO$_3$ solutions showing the effect of aging on the electrosorption capacity of carbon aerogel electrodes. Salt removal at cell voltages ranging from 0.6 to 1.2 V. Complete recycle of a 4.0 L volume of solution at a rate of 1 L/min. Data for new electrodes are represented 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.