JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 1007–1018

Capacitive deionization of NH_4ClO_4 solutions with carbon aerogel electrodes

J. C. FARMER, D. V. FIX, G. V. MACK, R. W. PEKALA, J. F. POCO

Lawrence Livermore National Laboratory, PO Box 808, Livermore, CA 94551, USA

Received 4 October 1995; revised 22 January 1996

A process for the capacitive deionization of water with a stack of carbon aerogel electrodes has been developed by Lawrence Livermore National Laboratory (LLNL). Unlike ion exchange, one of the more conventional deionization processes, no chemicals are required for regeneration of the system. Electricity is used instead. An aqueous solution of NH_4ClO_4 is pumped through the electrochemical cell. After polarization, NH_4^+ and ClO_4^- ions are removed from the water by the imposed electric field and trapped in the extensive cathodic and anodic double layers. This process produces one stream of purified water and a second stream of concentrate. The effects of cell voltage, salt concentration, and cycling on electrosorption capacity have been studied in detail.

1. Introduction

Hot water can be used to dissolve ammonium perchlorate (NH_4ClO_4) in solid rocket propellants during decommissioning. This process requires that dissolved NH_4ClO_4 be separated from the water so that the water can be recycled. As a result of this need, the feasibility of using capacitive deionization (CDI) with carbon aerogel electrodes to treat aqueous solutions of NH_4ClO_4 has been investigated. Solutions were passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to $1100\,m^2\,g^{-1}$) and very low electrical resistivity ($\leqslant 40\,m\Omega$ cm). After polarization, nonreducible and nonoxidizable ions were removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes. As desired, the effluent from the cell was a stream of purified water. Comparative experiments with NaCl were also conducted. 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. Carbon aerogel 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 so that no secondary waste is generated. In contrast to thermal processes such as evaporation, carbon aerogel CDI is much more energy efficient. Since no membranes or high pressure pumps are required, carbon aerogel CDI offers operational advantages over electrodialysis and reverse osmosis (RO).

2. Background

Several publications and patents have appeared that discuss the use of porous electrodes for the recovery of heavy metals from aqueous solutions by electrodeposition [1–8]. The first studies on CDI appear to have been published at the University of Oklahoma in the early 1960s [9, 10]. The application of interest was desalination of brackish water. The detailed report by Caudle *et al.* describes flow-through capacitors with porous, activated-carbon electrodes [10]. Inert polymeric binders were used to hold the carbon particles together in thin conductive sheets. Johnson *et al.* conducted similar studies of reversible electrosorption, or CDI, with beds of activated carbon [11–13]. Their experimental programme included verification of the theoretical basis for the 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 the study. Work on CDI was done in Israel several years later [15–17]. A column was built from two separated vertical beds of activated carbon, one serving as the anode and the other as the cathode. Concentration ratios as high as 1/100 were attained between the top and the bottom of the column. More recently, additional patents on CDI with activated carbon electrodes have appeared [18–20]. Work on CDI with carbon aerogel, a material developed by LLNL, has also been published [21–24].

0021-891X

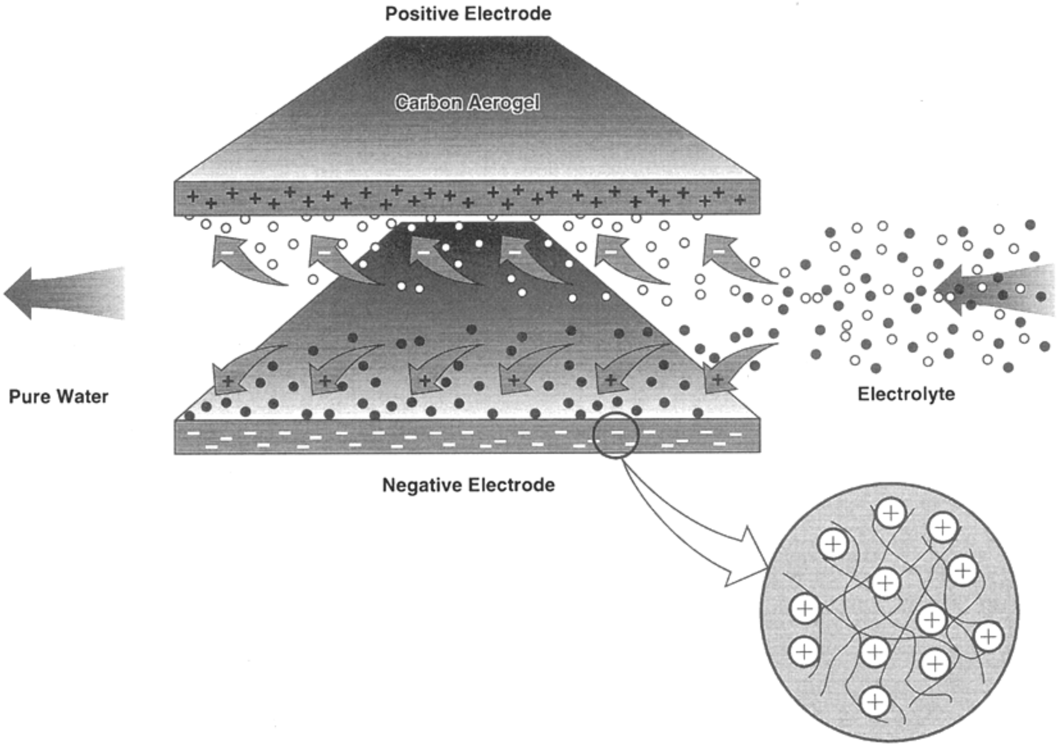

Fig. 1. Schematic diagram illustrating the principle of capacitive deionization with carbon aerogel electrodes. Cations and anions are held in the electric double layers formed at the cathode and anode, respectively. The high specific surface area of the carbon aerogel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes.

Several practical problems are encountered with conventional activated carbon CDI systems. For example, polymeric binders occlude significant fractions of the activated carbon surface [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 to prevent 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 is flown in the axial direction through the beds, a large pressure drop develops. Unfortunately, activated carbons appropriate for use in beds with low pressure drop also have relatively low specific surface areas. Furthermore, 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 [25–30]. However, none of these devices were designed to permit electrolyte flow and most required membranes to physically separate the electrodes.

The unique optical, thermal, acoustic, mechanical, and electrical properties of aerogels are directly related to their unusual nanostructure, which is composed of interconnected particles with microscopic interstitial pores [31–35]. Carbon aerogel is an ideal electrode material because of its low electrical resistivity ($\leqslant 40$ mΩ cm), high specific surface area (400 to 1100 m^2 g^{-1}), and controllable pore size distribution ($\leqslant 50$ nm). The exceptionally high conductivity of carbon aerogel, in contrast to loosely bonded carbon powders or activated carbon fibre cloths (ACFCs), is attributable to its monolithic structure which is composed of interconnected, covalently-bonded carbon particles ($\sim$12 nm dia.). Electrical conduction takes place by the drift of delocalized charge carriers within carbon nano-filaments, as well as by the transfer of carriers from one large conducting segment to another by hopping or tunnelling. In contrast to electrodes made from activated carbon powders and fibres, the activation energy for carrier transport in carbon aerogel is relatively small. As a result of these desirable characteristics, carbon aerogels have already been used as electrodes in supercapacitors with high energy and power densities [29].

3. Experimental details

This paper discusses the CDI of aqueous solutions of NH_4ClO_4 with carbon aerogel electrodes. Separation of other electrolytes by this process is discussed elsewhere [21–24]. Conceptually, the CDI process is very simple. After application of a voltage between two adjacent electrodes, cations and anions are drawn towards

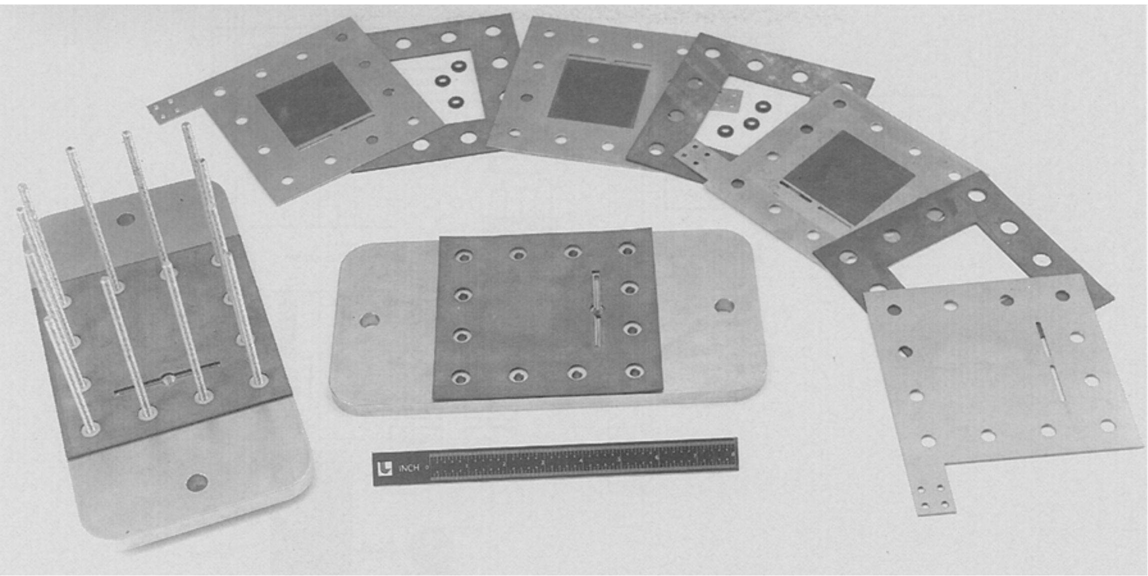

Fig. 2. Photograph showing a lower stainless steel header with a rubber gasket and threaded rods; an array of electrodes, gaskets and spacers; and an upper stainless steel header.

the cathode and anode, respectively (Fig. 1). These ions are held in the electric double layers formed at the extensive surfaces of the carbon aerogel electrodes until the voltage is reduced.

Electrodes were made from thin sheets of a carbon aerogel composite (CAC). The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [31–35]. Sheets of CAC were formed by infiltrating a 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 pyrolysed at 1050 °C in a nitrogen atmosphere to give thin sheets of CAC ($\sim 125\,\mu m$ thick) having bulk densities of $\sim 0.6\,g\,cm^{-3}$. 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 h at 85 °C. As previously discussed, this fabrication process results in unique, open-cell carbon foams that consist of interconnected, fibrous chains of colloidal-like particles with characteristic diameters of $\sim 12\,nm$. These materials have high porosities, high specific surface areas, and ultrafine pore sizes. The porosity and surface area 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 materials 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 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 electrosorption capacity in relatively small volumes.

Double-sided electrodes were made by gluing two sheets of CAC to both sides of a titanium plate that served as both a current collector and a structural support for the CAC. Each sheet of CAC was $6.86\,cm \times 6.86\,cm \times 0.0127\,cm$ and had a total active surface of approximately $2.8 \times 10^6\,cm^2$. As shown in Fig. 2, two orifices were located along one edge of each CAC sheet to admit water to the downstream electrode gap. A pattern of holes was located around the perimeter of the plate and accommodated 12 threaded rods that held 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 were assembled into a stack. Even electrodes served as cathodes while odd electrodes served as anodes. The electrodes and headers were aligned by the threaded rods. An electrode separation of 0.12–0.16 cm was maintained by cylindrical Delvin spacers concentric with the threaded rods and a rubber compression seal. Since the orifices in each electrode alternated from one side of the stack to the other, the flow path through the stack was serpentine. A stack of 384 pairs of carbon aerogel electrodes (384 double-sided electrodes) had a total active surface area of approximately $2.2 \times 10^9\,cm^2$. As shown in Fig. 3, flow through the stack was generated by a programmable, magnetically-coupled, screw pump with a 304 stainless steel head. The pressure drop across a stack of

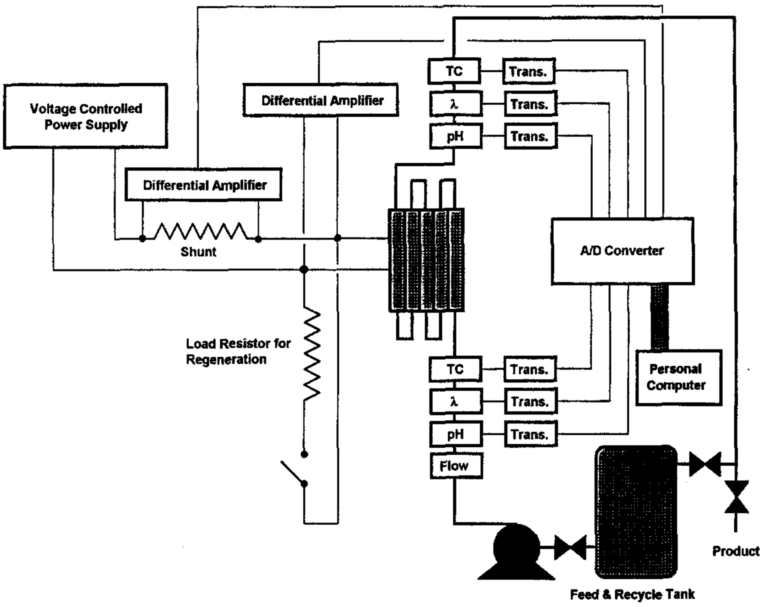

Fig. 3. Schematic diagram showing the apparatus used for demonstration of the capacitive deionization process.

48 electrode pairs was only 0.35 kg cm^{-2} (5 psi) at 1.7 dm^3 min^{-1}, whereas the drop across a stack of 384 electrode pairs was less than 1.96 kg cm^{-2} (28 psi) at 1.5 dm^3 min^{-1}. All lines were made of Teflon and had a nominal diameter of 0.635 cm (1/4 inch). The cells are polarized by programmable power supplies with a voltage range of 0 to 12 V or a current range of 0 to 60 A. Sensors were placed on the inlet and outlet lines of the cell so that electrical conductivity, pH, and temperature could be continuously monitored. A computerized data acquisition system logged important operating parameters such as voltage, current, conductivity, pH, and temperature. The data acquisition system was based on an Intel 486DX-33 microprocessor, a National Instruments 8-channel A/D converter, and LabTech Notebook data acquisition software for Microsoft® Windows™.

Parametric studies were performed with solutions of NH_4ClO_4 and NaCl in water. Conductivities were either 100 or 1000 μS cm^{-1} and voltage levels were 0.6, 0.8, 1.0, and 1.2 V. This range of solution conductivity was sufficiently high to be of practical interest, yet low enough to allow development of well defined breakthrough curves. Batch-mode experiments were done by continuously recycling either 2.0 or 4.0 dm^3 of electrolyte at a flow rate of 1.0 dm^3 min^{-1}. Single-pass experiments were done by pumping 20 dm^3 of electrolyte through the electrode stack at flow rate of 25 ml min^{-1}. In this case, there was no recycle.

4. Results

Overall, tests demonstrated that CDI with carbon aerogel can effectively remove NH_4ClO_4 and NaCl from water. Deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentrations and conductivities of NH_4ClO_4 and NaCl solutions were cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, for example, the electrosorption capacity, had a strong dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.6 V. Breakthrough was observed during single-pass experiments without recycle.

4.1. *Small stack with 48 electrode pairs and 100 μS cm^{-1} solutions*

Voltage, current, and solution conductivity data were collected while periodically charging and discharging a stack of 48 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 either NH_4ClO_4 or NaCl in water and had an initial conductivity of 100 μS cm^{-1}. Data for NaCl have been reported previously and are provided here for comparison [24]. During these batch-mode, fixed-volume experiments *with complete recycle*, the amplitude of the applied voltage pulse ranged from 0.6 to 1.2 V, the volume of electrolyte was 2.0 dm^3, and the flow rate through the stack of electrodes was 1.0 dm^3 min^{-1}. The salt concentration dropped when the electrodes were polarized, due to the trapping of anions and cations by the electric field present at aerogel–electrolyte interfaces, thereby forming extensive electric double layers. The outlet conductivity responded more quickly to cell polarization than the inlet conductivity, which is reasonable. As illustrated by Fig. 4, the concentration of the NH_4ClO_4 solution dropped to approximately 50 μS cm^{-1} after approximately 30 min of deionization, a reduction of solution conductivity and concentration of approximately 52%. The perchlorate capacity of the cell was 2.2×10^{-5} equivalents per gram of carbon, based on the mass of both anodes and cathodes, at an equilibrium concentration of

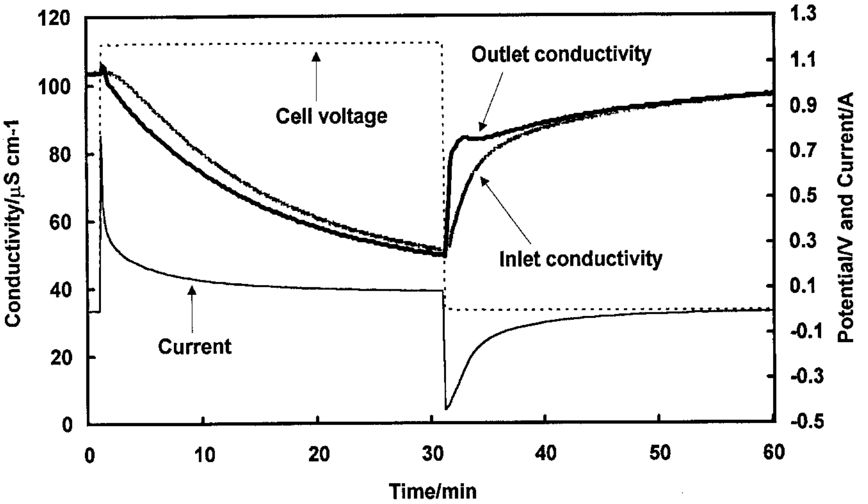

Fig. 4. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 2.0 dm^3 at a rate of 1.0 dm^3 min^{-1}. The apparatus included 48 aged electrode pairs operated at a cell voltage of 1.2 V.

0.33×10^{-3} equivalents per litre of solution. Immediately following this experiment, an identical experiment was conducted with NaCl. As shown in Fig. 5, a 57% reduction in solution conductivity and NaCl concentration was achieved. The chloride capacity of the cell was 3.6×10^{-5} equivalents per gram of carbon at an equilibrium concentration of 0.44×10^{-3} equivalents per litre of solution. Correcting for slight differences in equilibrium concentration, the capacity of the CAC electrodes to electrosorb large monovalent anions such as ClO_4^- was less than the capacity of these electrodes to electrosorb smaller anions like Cl^-. This observation is consistent with observed differences between NO_3^- and Cl^- capacities [22]. The salts were placed back into solution by discharging the cell. In the case of NH_4ClO_4, regeneration was more than 95% complete after about 30 min. The process was repeated for numerous cycles without any noticeable loss in capacity. The failure of the current to completely decay to zero was probably 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 with NH_4ClO_4 were also conducted at cell voltages of 0.6, 0.8, 1.0, and 1.2 V and are summarized in Table 1. Clearly, more ions are electrosorbed from solution at higher cell voltages.

4.2. *Expanded stack with 384 electrode pairs and 100 μS cm^{-1} solutions*

At a polarization of 1.2 V, a stack of 384 aged electrode pairs removed approximately 85% of the NH_4ClO_4 from a fixed 4.0 dm^3 volume of 100 μS cm^{-1} solution (Fig. 6). In a similar experiment with NaCl, 95% of the salt was removed (Fig. 7). Data for the deionization of 100 μS cm^{-1} NH_4ClO_4 solution at cell voltages of 0.6, 0.8, 1.0, and 1.2 V are compared in Fig. 8. Qualitatively, the results are similar to those for 48 aged electrode pairs. As the concentration of salt in the electrolyte diminished, the equilibrium surface charge density decreased, as expected.

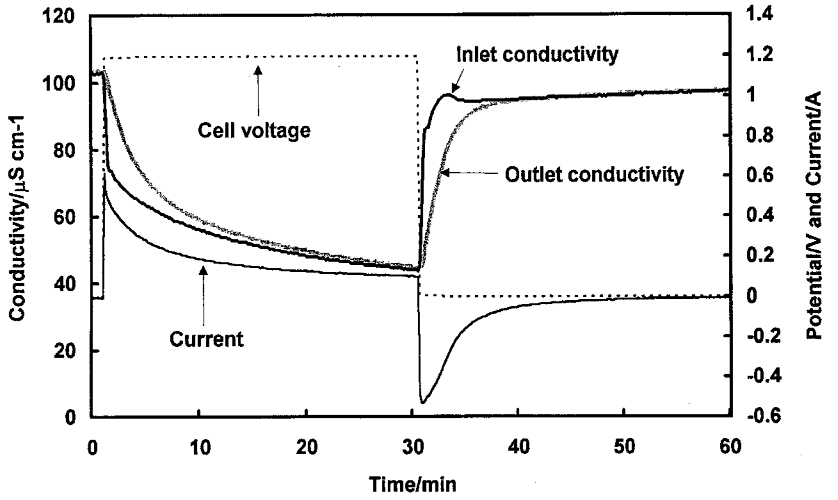

Fig. 5. Deionization of a fixed volume of 100 μS cm^{-1} NaCl solution. Conditions identical to those of Fig. 4.

Table 1. Actual data for carbon aerogel CDI of NH_4ClO_4 solutions

Reference	*Cell voltage* /V	*Initial conductivity* /μS cm^{-1}	*Final conductivity* /μS cm^{-1}	*Initial concentration* /ppm	*Final concentration* /ppm	*Initial concentration* × 10^3 /equiv. dm^{-3} solution	*Final concentration* × 10^3 /equiv. dm^{-3} solution	*NH_4ClO_4 removed* × 10^5 /equiv. g^{-1} carbon anode + cathode
Not shown	0.6	105	91	82	71	0.70	0.61	0.6
48 pairs	0.8	104	77	81	60	0.69	0.51	1.1
2 dm^3	1.0	100	67	78	53	0.67	0.45	1.3
1 dm^3 min^{-1}	1.2	98	50	77	39	0.65	0.33	2.0
Not shown	1.2 I	97	41	76	32	0.64	0.27	2.3
48 pairs	1.2	105	58	82	45	0.70	0.38	1.9
2 dm^3	1.2 R	102	31	80	24	0.68	0.20	2.9
1 dm^3 min^{-1}								
Fig. 8	0.6	99	74	77	58	0.66	0.49	0.3
384 pairs	0.8	101	50	79	39	0.67	0.33	0.5
4 dm^3	1.0	99	30	77	24	0.66	0.20	0.7
1 dm^3 min^{-1}	1.2	106	13	83	10	0.71	0.84	1.0
Fig. 10	0.6	997	883	779	690	6.63	5.87	1.2
384 pairs	0.8	1015	798	794	624	6.76	5.31	2.2
4 dm^3	1.0	1026	695	802	543	6.83	4.62	3.4
1 dm^3 min^{-1}	1.2	1026	625	802	489	6.83	4.16	4.1
	1.2 I	975	522	762	408	6.49	3.47	4.6

Note: I = initial performance; R = performance after rejuvenation by voltage reversal

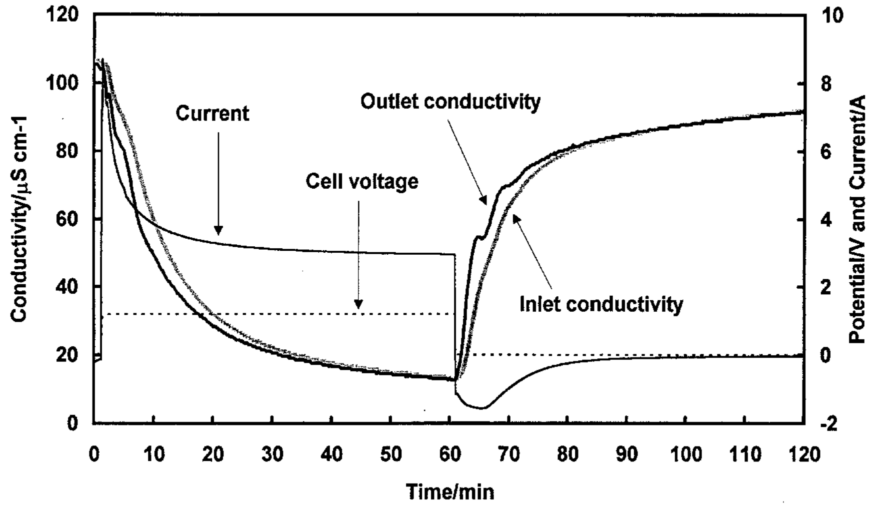

Fig. 6. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 dm^3 at a rate of 1.0 dm^3 min^{-1}. The apparatus included 384 aged electrode pairs operated at a cell voltage of 1.2 V.

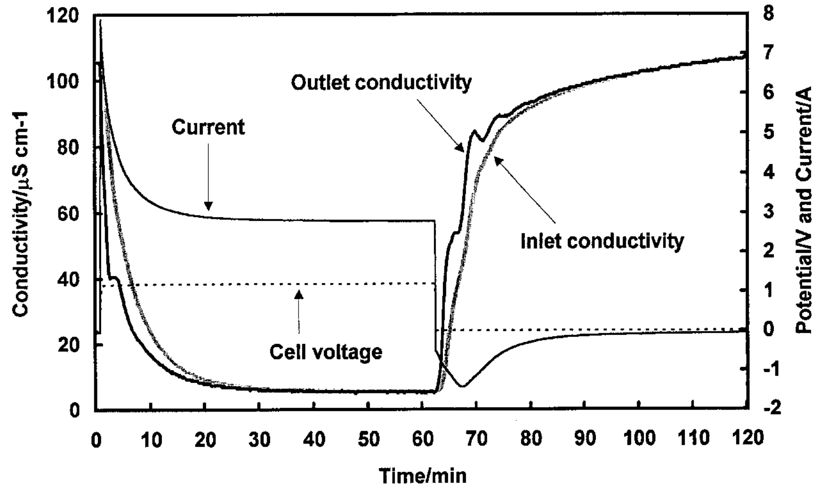

Fig. 7. Deionization of a fixed volume of 100 μS cm^{-1} NaCl solution. Conditions identical to those of Fig. 6.

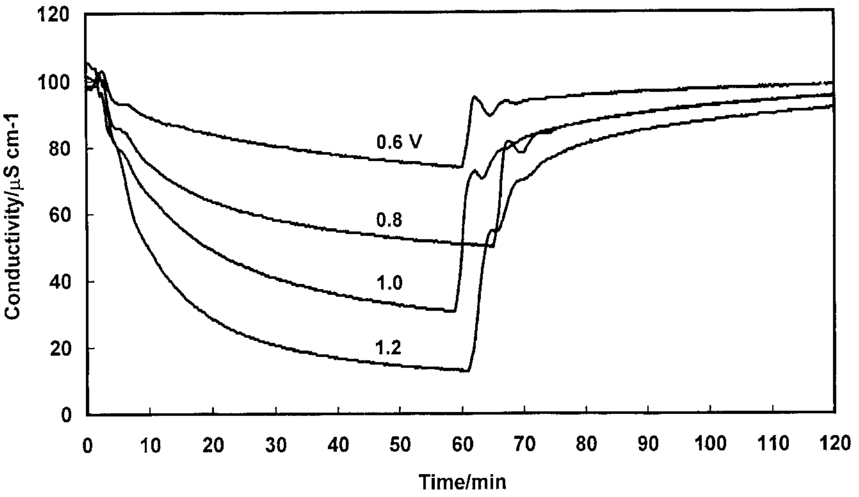

Fig. 8. Deionization of a fixed volume of 100 $\mu S\,cm^{-1}$ NH_4ClO_4 solution. Complete recycle of 4.0 dm^3 at a rate of 1.0 $dm^3\,min^{-1}$. The apparatus included 384 aged electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

4.3. *Rejuvenation of aged electrodes*

The loss of electrosorption capacity of carbon aerogel electrodes has been observed during prolonged operation [24]. Fortunately, such losses can be substantially recovered by reversal of the cell voltage. 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. Rejuvenation can be used to increase the electrosorption capacity of aged electrodes to levels approaching those achieved initially. The rejuvenation of 384 aged electrode pairs is illustrated by Fig. 9. The 'initial' conductivity transient is before rejuvenation whereas the 'after reversal' transients are after rejuvenation. In this case, such operation increased the removal of NH_4ClO_4 from 79% to 94%. It appears that such rejuvenation can be repeated numerous times with essentially the same desirable result.

4.4. *Expanded stack with 384 electrode pairs and 1000 $\mu S\,cm^{-1}$ solutions*

Transients in conductivity during batch-mode experiments with 1000 $\mu S\,cm^{-1}$ NH_4ClO_4 solution at four different applied voltages, 0.6, 0.8, 1.0, and 1.2 V, are shown in Fig. 10. Data are summarized in Table 1. 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 0.6 V. Electrosorption capacity decreased as the cell voltage was lowered. From these data it is concluded that a stack of 384 pairs of aged carbon aerogel electrodes polarized at 1.2 V has sufficient electrosorption capacity to remove 50% of the salt from a fixed, 4.0 dm^3 volume of 1000 $\mu S\,cm^{-1}$ NH_4ClO_4 solution. The effect of electrode ageing are apparant in the comparison of the transient for 1.2 V to one obtained during the initial test with the cell.

4.5. *Single-pass experiments with NH_4ClO_4 solutions*

Conductivity transients observed during a single-pass experiment with a 100 $\mu S\,cm^{-1}$ solution of NH_4ClO_4 and 48 electrode pairs are shown in Fig. 11. A similar experiment with 384 electrode pairs is shown in Fig. 12. The amplitude of the applied voltage was 1.2 V and the flow rate was 25 ml min^{-1}. In the

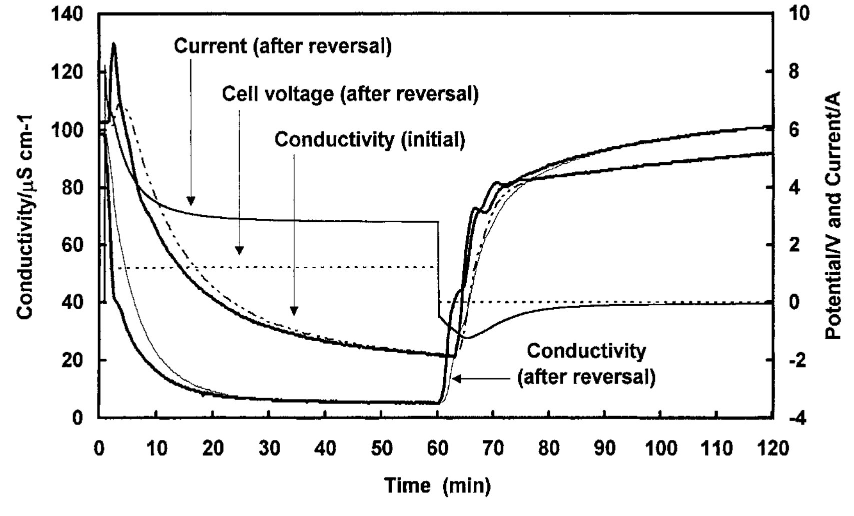

Fig. 9. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. All experiments at 1.2 V. Other conditions identical to those of Fig. 8.

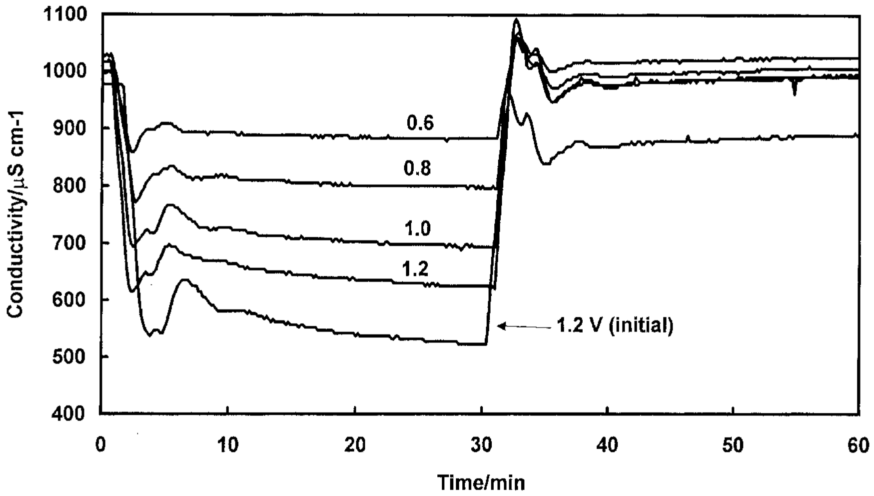

Fig. 10. Deionization of a fixed volume of 1000 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 dm^3 at a rate of 1.0 dm^3 min^{-1}. The apparatus included 384 aged electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

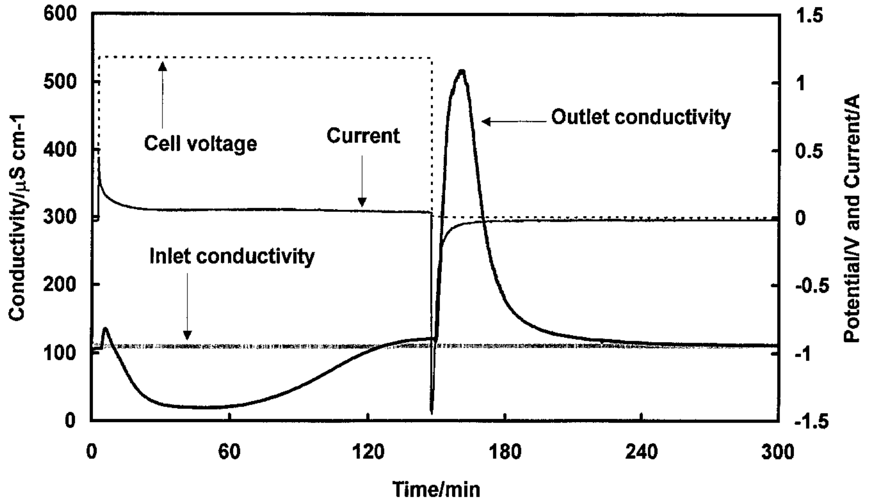

Fig. 11. Single-pass experiment with 100 μS cm^{-1} NH_4ClO_4 solution at a flow rate of 25 ml min^{-1}. The apparatus included 48 electrode pairs operated at cell voltage of 1.2 V.

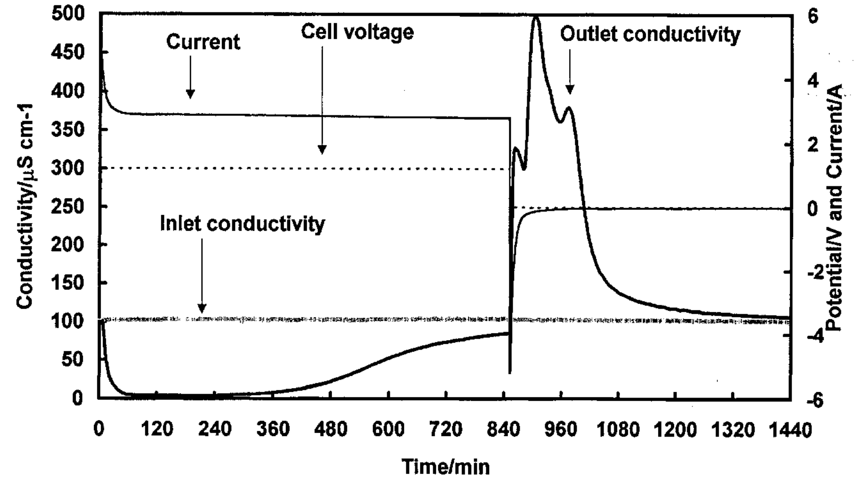

Fig. 12. Single-pass experiment with 100 μS cm^{-1} NH_4ClO_4 solution at a flow rate of 25 ml min^{-1}. The apparatus included 384 electrode pairs operated at cell voltage of 1.2 V.

experiment with 48 electrode pairs, the conductivity dropped to a level below 20 μS cm^{-1} after application of a voltage of 1.2 V across adjacent electrodes. Breakthrough was observed after the carbon aerogel became saturated with NH_4ClO_4, behaviour analogous to that of an ion exchange column. The mean time to breakthrough (τ), which is defined as the time required for the outlet concentration to reach 50% of the inlet concentration, was approximately 85 min. The cell was completely saturated at 120 min and regenerated by

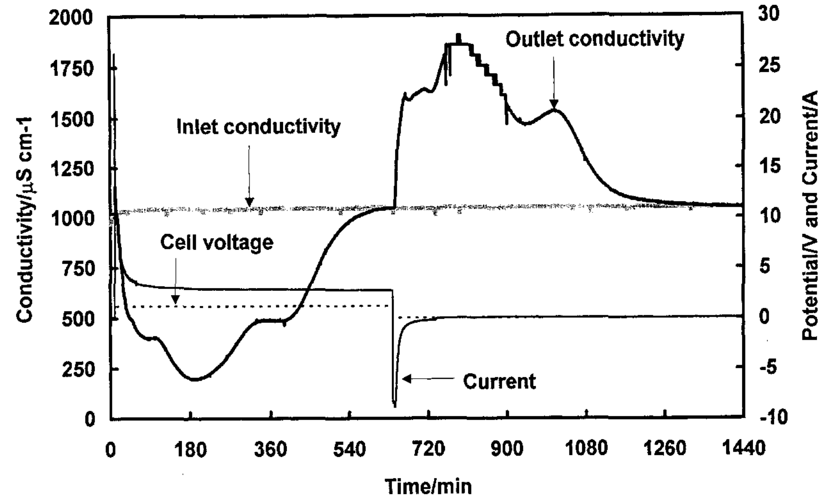

Fig. 13. Single-pass experiment with 1000 μS cm^{-1} NH_4ClO_4 solution at a flow rate of 25 ml min^{-1}. The apparatus included 384 electrode pairs operated at cell voltage of 1.2 V.

electrical discharge at 150 min, at which time the effluent concentration peaked at a level five times (5×) greater than the feed concentration. Since τ should be proportional to active surface area, an increase in the number of electrode pairs from 48 to 384 was expected to increase τ by a factor of eight (8×). As shown in Fig. 12, τ was approximately 600 min in experiments with 384 electrode pairs, an increase of only seven times (7×). The failure of τ to scale linearly with the number of electrode pairs may be due to (i) unexpectedly low active surface area of additional electrode pairs and (ii) axial mixing of electrolyte along the flow path through the cells. Conductivity transients during a single-pass experiment in a 1000 μS cm^{-1} solution of NH_4ClO_4 and 384 electrode pairs are shown in Fig. 13. The conductivity dropped to a low of 250 μS cm^{-1} after application of a voltage of 1.2 V across adjacent electrodes. The concentration stayed below 500 μS cm^{-1} for 420 min, representing a salt removal of about 50% during that period of time.

5. Analysis of data

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 [36]. In the case of dilute aqueous solutions at 25 °C, the following expression should be obeyed by both anodes and cathodes:

$$\sigma = 11.7\sqrt{C}\,\sinh(19.5 z\phi_0) \qquad (1)$$

Note that σ is the surface charge density (μC cm^{-2}), C is the electrolyte concentration (mol dm^{-3}), z is the ionic charge, and ϕ_0 is the electrode potential (mV). However, double layer formation on carbon electrodes is much more complicated. For example, cathode capacities are much higher than corresponding anode capacities [9, 10]. This is attributed to the cation affinity of carbonyl groups on the electrode surface. Therefore, the electrosorption capacity of an electrochemical cell built with porous carbon electrodes is probably limited by its ability to accomodate anions.

Data from the experiments with NH_4ClO_4 are summarized in Table 1. Multiple variable regression analysis [37] of this data, excluding the second group for 48 electrode pairs, was used to determine the dependence of the anion capacity, Y, on equilibium electrolyte concentration, X_1, and cell voltage, X_2.

$$Y = 1.7321\,X_1^{0.4331}X_2^{2.3682} \qquad (2)$$

where Y has the units of 10^{-5} equivalents per gram of carbon aerogel (both anode and cathode), X_1 has the units of 10^{-3} equivalents per litre of solution, and X_2 is given in volts. As shown in Table 2, the agreement between experiment and data is very good. This is reflected in the calculated multiple-variable regression coefficient, R^2, which is 0.921. Since Y and X_1 are directly proportional to σ and C, respectively, one could reasonably expect:

$$Y \propto X_1^{0.5} \qquad (3)$$

It is believed that the failure to observe square root concentration dependence is due to self-shielding effects experienced by the porous carbon electrodes. Values of Y are predicted at 0.03 N so that they can be easily compared with anion capacities published for other systems [9, 10]. The highest value in Table 2 is 19×10^5 equivalents per gram of carbon aerogel at 1.2 V and 0.03 N. This extrapolated value is based on data obtained after rejuvenation by voltage reversal. The mass specific chloride capacities published 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. Chloride capacities for carbon aerogel electrodes at 1.2 V and 0.03 N are in the range of 5 to 30 equivalents per gram of carbon, based on the anode mass alone. Here too it appears that perchlorate capacities for carbon aerogel electrodes are less than chloride capacities published for both activated carbon [9, 10] and carbon aerogel

Table 2. Regression analysis of data for carbon aerogel CDI of NH_4ClO_4 solutions

Reference	*Independent variables*		*Dependent variable: NH_4ClO_4 removed (equiv. g^{-1} carbon) $\times 10^5$*				
	Voltage /V	*Equilib. conc.* /(equiv. dm^{-3}) $\times 10^3$	*Observed at equilib. conc.**	*Prediction at equilib. conc.**	*Prediction at conc. of 0.03 N**	*Prediction at conc. of 0.03 N†*	*Extrapolated to conc. of 0.03 N†*
Not shown	0.6	0.61	0.6	0.4	0.8	1.7	2.2
48 pairs	0.8	0.51	1.1	0.8	1.6	3.3	4.8
2 dm^3	1.0	0.45	1.3	1.2	2.8	5.6	6.0
1 dm^3 min^{-1}	1.2	0.33	2.0	1.7	4.3	8.6	1.0
Not shown	1.2 I	0.27	2.3	1.5	4.3	8.6	1.3
48 pairs	1.2	0.38	1.9	1.8	4.3	8.6	9.4
2 dm^3	1.2 R	0.20	2.9	1.3	4.3	8.6	19
1 dm^3 min^{-1}							
Fig. 8	0.6	0.49	0.3	0.4	0.8	1.7	1.1
384 pairs	0.8	0.33	0.5	0.6	1.6	3.3	2.7
4 dm^3	1.0	0.20	0.7	0.9	2.8	5.6	4.5
1 dm^3 min^{-1}	1.2	0.84	1.0	0.9	4.3	8.6	8.9
Fig. 10	0.6	5.87	1.2	1.1	8.3	1.7	1.7
384 pairs	0.8	5.31	2.2	2.1	1.6	3.3	3.4
4 dm^3	1.0	4.62	3.4	3.4	2.8	5.6	5.6
1 dm^3 min^{-1}	1.2	4.16	4.1	4.9	4.3	8.6	7.1
	1.2 I	3.47	4.6	4.6	4.3	8.6	8.6

Note: I = initial performance; R = performance after rejuvenation by voltage reversal.

* Anode + cathode.

† Anode alone.

Table 3. NH_4ClO_4 capacity of carbon cerogel electrodes

Feed concentration /ppm	*Feed concentration* /(equiv. dm^{-3}) $\times 10^3$	*Salt capacity at 0.6 V* /(equiv. g^{-1} carbon anode + cathode) $\times 10^5$	*Salt capacity at 1.2 V* /(equiv. g^{-1} carbon anode + cathode) $\times 10^5$	*Feed capacity at 0.6 V* /(dm^3 g^{-1} carbon anode + cathode) $\times 10^3$	*Feed capacity at 1.2 V* /(dm^3 g^{-1} carbon anode + cathode) $\times 10^3$
10	0.0851	0.18	0.92	21	110
100	0.851	0.48	2.5	5.7	29
1000	8.51	1.3	6.7	1.5	7.9
10 000	85.1	3.5	18	0.42	2.2
35 000	298	6.1	32	0.21	1.1
50 000	426	7.1	37	0.17	0.86
75 000	638	8.5	44	0.13	0.69

Table 4. Theoretical minimum energy required for removal of NH_4ClO_4 by carbon aerogel CDI

Feed conc. /ppm	W_{min} /J mol^{-1}	*QV/2 at 0.6 V* /J mol^{-1}	*QV/2 at 1.2 V* /J mol^{-1}	W_{min} /Wh gal^{-1}	*QV/2 at 0.6 V* /Wh gal^{-1}	*QV/2 at 1.2 V* /Wh gal^{-1}
10	2.9×10^{-2}	4.0×10^{-2}	8.0×10^{-2}	1.7×10^{-3}	2.3×10^{-3}	4.7×10^{-3}
100	2.4×10^{-1}	4.4×10^{-1}	8.8×10^{-1}	1.4×10^{-2}	2.6×10^{-2}	5.1×10^{-2}
1000	1.6	4.5	9.0	9.5×10^{-2}	2.6×10^{-1}	5.2×10^{-1}
10 000	8.9	50	99	5.2×10^{-1}	2.9	5.8
35 000	20	250	490	1.2	14	29
50 000	25	470	940	1.4	27	55
75 000	31	1600	3200	1.8	90	190

[24]. Table 3 gives estimates of the amount of NH_4ClO_4 contaminated water that can be treated with a given mass of carbon aerogel before regeneration. For example, 1000 g of CAC is sufficient to treat 29 dm^3 of 100 ppm NH_4ClO_4 solution. From values of τ deduced from Figs 11 and 12, it is concluded that 1000 g of CAC is sufficient to treat 57 to 65 dm^3 of 100 ppm solution. The discrepancy may be due to differences in electrode service (time since rejuvenation). Values in Table 3 appear to be conservative. Note that values of 'NH_4ClO_4 removed' in Tables 1 and 2 require knowledge of the total carbon mass of the electrodes. Based upon the average weight of several representative electrodes, 48 pairs were estimated to have a mass of 32.8 g and 384 pairs were estimated to have a mass of 262.7 g.

Estimates of the minimum energy requirements of the process are given in Table 4. The minimum theoretical work required by an isothermal process to separate a 1000 ppm NH_4ClO_4 solution into a 1 ppm product stream and a 95 000 ppm concentrate stream is approximately 1.6 J mol^{-1} (0.1 Wh gal^{-1}), assuming that the NH_4ClO_4 obeys the Debye-Huckel activity coefficient model [38, 39]. The minimum electrical energy required for charging a CDI cell with NH_4^+ and ClO_4^- is 4.5 J mol^{-1} (0.26 Wh gal^{-1}) at 0.6 V and 9.0 J mol^{-1} (0.52 Wh gal^{-1}) at 1.2 V. These values correspond to $QV/2$ where Q is the stored electrical charge and V is the cell voltage. In real systems, ohmic losses and finite pressure drops lead to energy requirements above these limiting values. However, energy recovery by a second device operating in parallel can be used to substantially reduce the overall requirement, allowing CDI systems to more closely approach the theoretical minimum based on thermodynamics.

6. Discussion

The resistance of a typical 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 1–3 Ω [10], compared to ~10 μΩ for an aerogel electrode. The value for the aerogel electrode is based on a measured resistivity of 40 mΩ cm [31]. 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 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 Brunauer–Emmet–Teller (BET) surface areas as high as 3000 m^2 g^{-1} 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 nitrogen 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 [36]. In the case of a 1 : 1 electrolyte in water at 25 °C, the characteristic thickness of the diffuse layer ranges from 1 nm at a concentration of 10^{-1} M to 30 nm at 10^{-4} M. Finally, published capacitance–density data indicates that the double layer at the carbon–electrolyte interface is primarily formed in the mesopore region [31].

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 are 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.

Note that the product purity that can be achieved with carbon aerogel CDI is limited by the number of electrode pairs. In a separation process, the highest purity is achieved with infinite theoretical stages.

7. Conclusions

The CDI of aqueous solutions of NH_4ClO_4 with carbon aerogel electrodes has been demonstrated for the first time. Cell voltages ranging from 0.6 to 1.2 V were investigated. The best performance (salt removal) was achieved at 1.2 V. In single-pass experiments with 384 electrode pairs, approximately 95% of the NH_4ClO_4 in a 100 μS cm^{-1} feed stream was removed until saturation of the carbon aerogel electrodes was reached. The capacity of carbon aerogel anodes to electrosorb ClO_4^-, a relatively large monovalent anion, is less than the capacity of these anodes to electrosorb Cl^-. Similar trends have been observed during comparative experiments with NO_3^- and Cl^-. In general, electrosorption capacity decreases with cycle life. Fortunately, it appears that most of the loss in capacity can be recovered by periodically reversing the electrode polarization (rejuvenation). Additional studies should be performed so that the effect of electrode ageing on ClO_4^- capacity can be quantified more precisely. Carbon aerogel CDI offers several potential advantages over conventional thermal and membrane processes for water treatment and deserves further investigation.

Acknowledgements

These studies with NH_4ClO_4 were sponsored by the Environmental Compliance Division of Armstrong Laboratories at Tyndall Air Force Base, Florida. The Program Manager was Lt. Ray Anthony Smith. Original development of the carbon aerogel CDI process was made possible by funding provided by the Strategic Environmental Research and Development (SERDP) Program. This work was done under the auspices of the US Department of Energy (DOE) by LLNL under contract W-7405-Eng-48.

References

[1] J. A. Trainham and J. Newman, *J. Electrochem. Soc.* **124** (1977) 1528–40.
[2] J. Van Zee and J. Newman, *ibid.* **124** (1977) 706–8.
[3] K. Moeglich, *US Patent 4 072 596*, 7 Feb. (1978).
[4] W. J. Blaedel and J. C. Wang, *Anal. Chem.* **51** (1979) 799–802.
[5] T. Risch and J. Newman, *J. Electrochem. Soc.* **131** (1984) 2551–6.
[6] P. Lessner and J. Newman, *ibid.* **131** (1984) 1828–31.
[7] G. F. Platek, *US Patent 4 515 672*, 7 May (1985).
[8] M. Matlosz and J. Newman, *J. Electrochem. Soc.* **133** (1986) 1850–9.
[9] B. B. Arnold and G. W. Murphy, *J. Phys. Chem.* **65** (1961) 135–8.
[10] D. D. Caudle, J. H. Tucker, J. L. Cooper, B. B. Arnold and A. Papastamataki, 'Electrochemical Demineralization of Water with Carbon Electrodes', Research and Development Progress Report 188, US Department of the Interior, May (1966).
[11] A. M. Johnson, A. W. Venolia, J. Newman, R. G. Wilbourne, C. M. Wong, , W. S. Gillam, S. Johnson and R. H. Horowitz, 'Electrosorb Process for Desalting Water', Office of Saline Water Research and Development Progress Report 516, US Department of the Interior, Publication 200 056, March (1970).
[12] A. M. Johnson, A. W. Venolia, R. G. Wilbourne and J. Newman, 'The Electrosorb Process for Desalting Water', Marquardt Co., Van Nuys, CA, March (1970).
[13] A. M. Johnson, *US Patent 3 515 664*, 2 June (1970).
[14] A. M. Johnson and J. Newman, *J. Electrochem. Soc.* **118** (1971) 510–7.
[15] Y. Oren and A. Soffer,*ibid.* **125** (1978) 869–75.
[16] *Idem, J. Appl. Electrochem.* **13** (1983) 473–87.
[17] *Idem, ibid.* **13** (1983) 489–505.
[18] M. D. Andelman, *US Patent 5 415 768*, 16 May (1995).
[19] *Idem, US Patent 5 360 540,* 1 Nov. (1994).
[20] T. Otowa, *International Patent Appl. PCT/US94/05364*, 24 Nov. (1994).
[21] J. C. Farmer, *US Patent 5 425 858,* 20 June (1995).
[22] J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala and J. F. Poco, Proceedings of the 5th International Conference on Radiation Waste Management Environment Remediation, Berlin, Germany, 3–9 September (1995), American Society of Mechanical Engineers (ASME), New York, vol. 2, (1995) pp. 1215–20.
[23] J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala and J. F. Poco, Proceedings of the 1995 International SAMPE Technical Conference, Albuquerque, NM, 9–12 October (1995), Society for the Advancement of Material and Process Engineering (SAMPE), Covina, CA, vol. 27 (1995) pp. 294–304.
[24] J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala and J. F. Poco, *J. Electrochem. Soc.* **143** (1996) 159–69.
[25] Keitaro Katsu, Nippon Electric Co., *Japan Patent Appl. 91-303 689* (1991).
[26] Matsushita Electric Industrial Co., Ltd., *Japan Patent Appl. 83-89 451* (1983).
[27] J. Tabuchi, Y. Kibi, T. Saito and A. Ochi, 'Electrochemical Properties of Activated Carbon/Carbon Composites for Electric Double-layer Capacitor in New Sealed Rechargeable Batteries and Supercapacitors', presented at the 183rd Electrochemical Society Meeting, Honolulu, HI, 16–21 May (1993).
[28] Mitsui Petrochem Ind., *Japan Patent Appl. 89-210 642* (1989).
[29] S. T. Mayer, R. W. Pekala and J. L. Kaschmitter, *J. Electrochem. Soc.* **140** (1993) 446–51.
[30] F. M. Delnick, D. Ingersoll and D. Firsich, 'Double-layer Capacitance of Carbon Foam Electrodes', SAND-93-2681, Sandia National Laboratory, Albuquerque, NM (1993).
[31] R. W. Pekala, S. T. Mayer, J. F. Poco and J. L. Kaschmitter, 'Novel forms of carbon II', (edited by C. L. Renschler, D. M. Cox, J. J. Pouch and Y. Achiba), *MRS Symp. Proc.* **349** (1994) 79.
[32] J. Wang, L. Angnes, H. Tobias, R. A. Roesner, K. C. Hong, R. S. Glass, F. M. Kong and R. W. Pekala, *Anal. Chem.* **65** (1993) 2300–3.
[33] J. L. Kaschmitter, S. T. Mayer and R. W. Pekala, *US Patent 5 260 855*.
[34] R. W. Pekala, C. T. Alviso, 'Novel forms of carbon', (edited by C. L. Renschler, J. J. Pouch and D. M. Cox), *MRS Symp. Proc.* **270** (1992) 3.
[35] R. W. Pekala, 'Ultrastructure processing of advanced materials', (edited by D. R. Uhlmanjn and D. R. Ulrich), John Wiley & Sons, New York (1992) pp. 711–17.
[36] A. J. Bard and L. R. Faulkner, 'Electrochemical methods, fundamentals and applications', John Wiley & Sons, New York (1980) pp. 500–15.
[37] W. J. Dixon and F. J. Massey, Jr., 'Introduction to statistical analysis', 3rd edn., McGraw-Hill, San Francisco, CA (1969), chapter 11, pp. 193–6.
[38] C. J. King, 'Separation processes', 2nd edn., McGraw-Hill, San Francisco, CA (1980) pp. 661–4.
[39] J. S. Newman, 'Electrochemical systems', 2nd edn., Prentice Hall, Englewood Cliffs, NJ (1991) pp. 89–94.