AL/EQ-TR-1995-0038

ARMSTRONG LABORATORY

CAPACITIVE DEIONIZATION OF NH_4CLO_4 SOLUTIONS WITH CARBON AEROGEL ELECTRODES

Kevin T. McSweeney, Dave Morris, Bob Rettie,
Stephen E. Kelley

Department of Chemistry and Materials Science
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore CA 94551

ENVIRONICS DIRECTORATE
139 Barnes Drive, Suite 2
Tyndall AFB FL 32403-5323

August 1996

Final Technical Report for Period October 1994 - June 1995

AIR FORCE MATERIEL COMMAND
TYNDALL AIR FORCE BASE, FLORIDA 32403-5323

NOTICES

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any employees make any warranty, expressed or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness or any privately owned rights. Reference herein to any specific commercial process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency, contractor, or subcontractor thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency, contractor, or subcontractor thereof.

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligations, whatsoever. The fact that the Government may have formulated or in any way supplies the said drawings, specifications, or other data, is not to be regarded by implication, or otherwise in any manner construed, as licensing the holder or any person or corporation; or as conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

Ray A.

RAY A SMITH, 1LT, USAF, BSC
Project Manager

Allan M Wei

ALLAN M. WEINER, LT COL, USAF
Chief, Environmental Compliance Division

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE Aug. 15, 1996	3. REPORT TYPE AND DATES COVERED Final, Oct 94 - Jun 95

4. TITLE AND SUBTITLE
CAPACITIVE DEIONIZATION OF NH_4CLO_4 SOLUTIONS WITH CARBON AEROGEL ELECTRODES

5. FUNDING NUMBERS
PE: SERDP

6. AUTHOR(S)
MSgt Kevin T. McSweeney, Mr. Dave Morris, Bob Rettie, Stephen E. Kelley

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry and Materials Science,
Lawrence Livermore National Laboratory
7000 Eat Avenue, Livermore, Califormia 94551

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Armstron Laboratory Environics Directorate (AL/EQ)
139 Barnes Drive, Suite 2
Tyndall Air Force Base, Florida 32403-5319

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AL/EO-TR-1995-0038

11. SUPPLEMENTARY NOTES
AL/EQR Project Manager is LtRay Smith, DSN 523-6462 or (904) 283-6462

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE
A

13. ABSTRACT *(Maximum 200 words)*

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 electrosorption capacities for NH_4ClO_4 and NaCl have been investigated and are reported here.

14. SUBJECT TERMS
Amonium perchlorate (U), Carbon Aerogel (U), Capacitive Deionization (U)

15. NUMBER OF PAGES
58

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18

(The reverse of this page is blank.)

PREFACE

This report was prepared by the Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, 7000 East Avenue or P.O. Box 808 Livermore, California 94551 under contract No. W-7405-Eng-48. These studies were sponsored by the Armstrong Laboratory Environics Directorate (AL/EQ), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319. Original development of the carbon aerogel CDI process was made possible by funding provided by the Strategic Environmental Research and Development (SERDP) Program.

This final report describes a process for the capacitive deionization of water with a stack of carbon aerogel electrodes 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 electrosorption capacities for NH_4ClO_4 and NaCl were investigated.

The AL/EQS project manager was 1Lt Ray A. Smith, USAF, BSC.

Executive Summary

A process for the capacitive deionization (CDI) 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 electrosorption capacities for NH_4ClO_4 and NaCl have been investigated and are reported here.

Aqueous solutions of NH_4ClO_4 are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 $m^2\ g^{-1}$). After polarization, non-reducible and non-oxidizable ions are removed from the electrolyte by the imposed electric field and held in electric field and held in electric double layers formed at the surfaces of electrodes. The effluent from the cell is purified water. Regeneration is accomplished by electrically discharging the cell. This regeneration produces no secondary waste. Since no membranes or high pressure pumps are required, CDI offers operational advantages over electrodialysis and reverse osmosis.

TABLE OF CONTENTS

List of Figures

Figure Page

1. Introduction

Hot water can be used to dissolve ammonium perchlorate (NH_4ClO_4) in solid rocket propellants during decommisioning. This process requires that dissolved NH_4ClO_4 be separated from the water so that the water can be recycled. The capacitive deionization (CDI) of aqueous solutions of NH_4ClO_4 with a stack of carbon aerogel electrodes has been investigated by Lawrence Livermore National Laboratory and is reported here. Solutions are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m^2 g^{-1}). 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 desired, the effluent from the cell is purified water. Comparative experiments with NaCl have also been 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. 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).

2. 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 1960's [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 polymeric binders were used to hold the carbon particles together in thin conductive sheets. Johnson et al. conducted similar studies of reversible electrosorption, or capacitive deionization, with beds of activated carbon and published their work in early 1970's [11-13]. Their experimental program 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. Several years later, work on CDI was done in Israel and published in the 1980's [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 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 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 were designed to permit electrolyte flow and most required membranes to physically separate the electrodes. 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 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 (~7.5 kW kg^{-1}). Subsequently, a wide variety of microcellular carbon foams for application in double-layer capacitors were 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 m^2 g^{-1}), 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 $m^2 g^{-1}$) with a 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 and power densities [22, 25]. Carbon aerogels provide an almost ideal electrode material because of their low electrical resistivity ($\leq$ 40 mΩ-cm), controllable pore size distribution ($\leq$ 50 nm), and high volumetric surface areas (~ 500 $m^2 cm^{-3}$). 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 diameter). Electrical conduction takes place by both the drift of the delocalized charge carriers within these nano-filaments 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 partilces is relatively small in the carbon aerogels.

This paper discusses the capacitive deionization (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 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 electodes. To gain insight into electode 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 waste water in various industries. This process generates large volumes of corrosive secondary wastes that must be treated for disposal through regeneration processes. 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 HNO_3 become contaminated with PuO_2^{2+} and other radioisotopes. In this case, every kilogram of cation exchange resin requires approximately 100 kilograms of 10 wt. % HNO_3 and 2 to 3 kilograms of rinse water for regeneration. Similarly, every kilogram of used anion exchange resin requires approximately 100 kilograms of 10 wt. % NaOH and 2 to 3 kilograms 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 due to pitting and stress corrosion cracking. CDI could also be used to remove radioactive ions from the contaminated waste water of nuclear power plants before discharge. Deionizers based on columns of zeolite, silica gel, and ion exchange resins were evaluated for the removal ^{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.

3. Experimental

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. 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 600 to 800 m^2 g^{-1}. Each sheet of CAC is 6.86 cm x 6.86 cm x 0.0127 cm and has a total active surface of approximately 2.8 x 10^6 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 are located around the perimeter of the titanium plate and accommodate 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 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 384 pairs of carbon aerogel electrodes has a total active surface area of approximately 2.2 x 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^{-1}, whereas the drop across a stack of 384 electrode pairs is less than 1.96 kg cm^{-2} (28 psi) at 1.5 L min^{-1}. All lines are made of Teflon and have a nominal diameter of 0.635 cm (1/4 inch). 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. 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 voltage, current, conductivity, pH, and temperature. The data acquisition system is based on an Intel 486DX-33 microprocessor, a National Instruments 8-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 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 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 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. This fabrication process results in unique open-cell carbon foams that have high porosities, high specific surface areas (400 to 1100 m^2 g^{-1}), ultrafine cell and pore sizes (≤ 50 nm), and a solid matrix composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of ~12 nm. These quoted specific surface areas are based on Brunauer-Emmet-Teller (BET) analyses. The BET equation is an extension of the Langmuir adsorption 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: (1) the resorcinol/catalyst (R/C) ratio of the starting solution; (2) the pyrolysis temperature; and (3) 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 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.

Parametric studies were performed with solutions of NH_4ClO_4 and NaCl in water. In each case, experiments were performed over a broad range of solution conductivity and cell voltage. Conductivities were either 100 or 1000 $\mu S\ cm^{-1}$ ($\mu mho\ cm^{-1}$) and voltage levels were 0.6, 0.8, 1.0, and 1.2 V. Batch-mode experiments were done by continuously recycling either 2.0 or 4.0 L of electrolyte at a flow rate of 1.0 L min^{-1}. Single-pass experiments were done by pumping 20 L 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, e.g., 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. *Results with 48 electrode pairs and 100 $\mu S\ cm^{-1}$ 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 semi-continuously for several months. The electrolyte was a solution of either NH_4ClO_4 or NaCl in water and had an initial conductivity of 100 $\mu S\ cm^{-1}$. Data for NaCl have been reported previously and are provided here for comparison [34]. 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 L, and the flow rate through the stack of electrodes was 1.0 L/min. From the experiments with both NH_4ClO_4 and NaCl solution at 1.2 V, it is clear that the salt concentration drops when the electrodes are polarized. After approximately 30 minutes of deionization, the concentration of the NH_4ClO_4 solution dropped to approximately 50 $\mu S\ cm^{-1}$, a reduction of solution conductivity and concentration of approximately 50% (Fig. 1). The salt was placed back into solution by discharging the cell. The regeneration was more than 95% complete after about 30 minutes. The process was repeated for numerous cycles without noticeable loss in capacity. The failure of the current to completely decay 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. In an identical experiment with NaCl a 55% reduction in solution conductivity and concentration was achieved (Fig. 2). Similar experiments with NH_4ClO_4 were also conducted at cell voltages of 0.6, 0.8, 1.0, and 1.2 V. Transients in solution conductivity for all experiments are shown in Fig. 3. Clearly, more ions are electrosorbed from solution at higher cell voltages.

4.2. *Rejuvenation of aged electrodes*

Fortunately, as illustrated by Fig. 4, the electrosorption capacity lost with aging can be almost completely recovered by voltage reversal in the cell [34]. Such rejuvenation can be used to increase the electrosorption capacity of aged electrodes to levels near that achieved initially. In this case, such

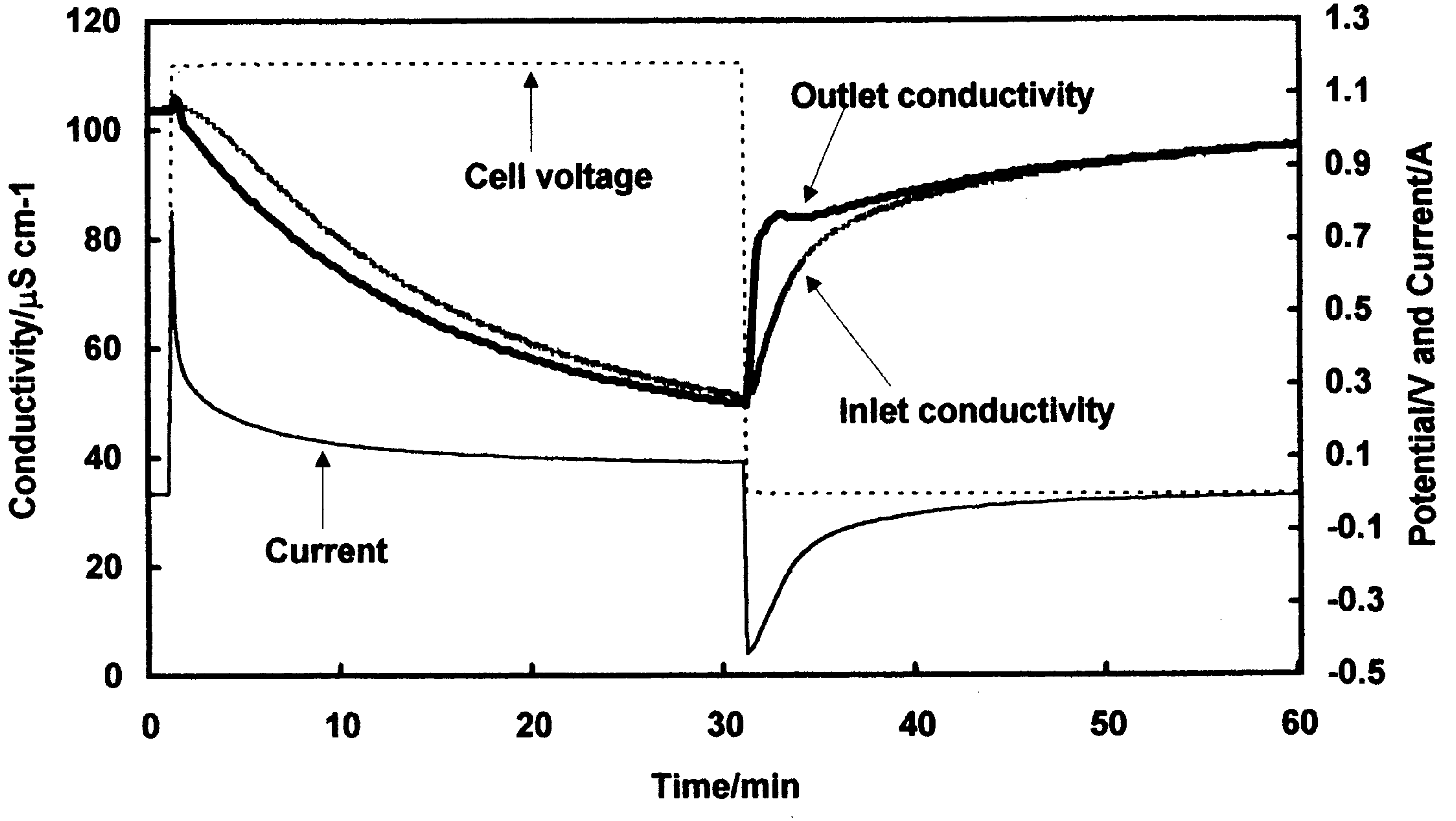

Fig. 1. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 aged electrode pairs operated at a cell voltage of 1.2 V.

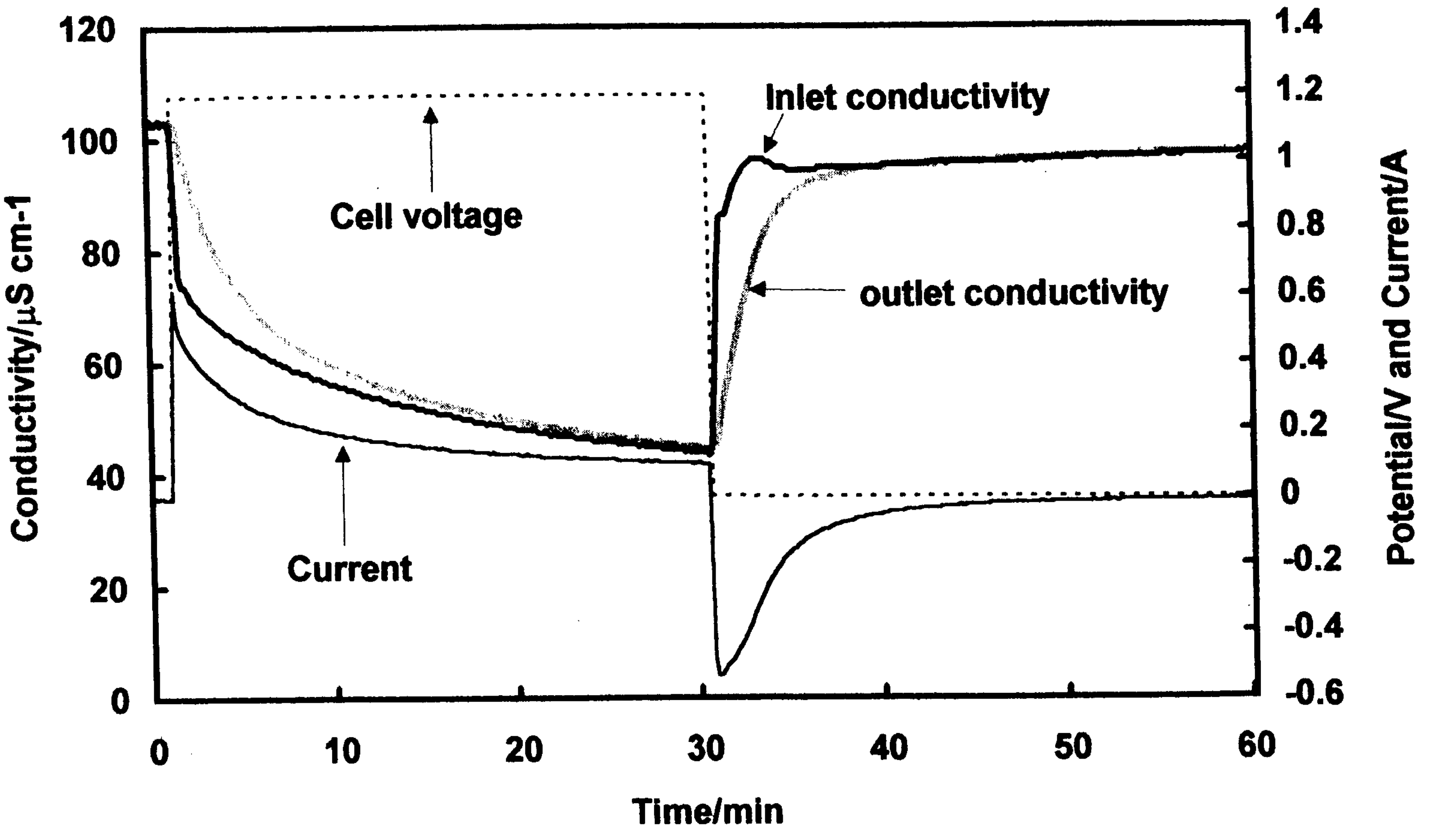

Fig. 2. Deionization of a fixed volume of 100 μS cm^{-1} NaCl solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 aged electrode pairs operated at a cell voltage of 1.2 V.

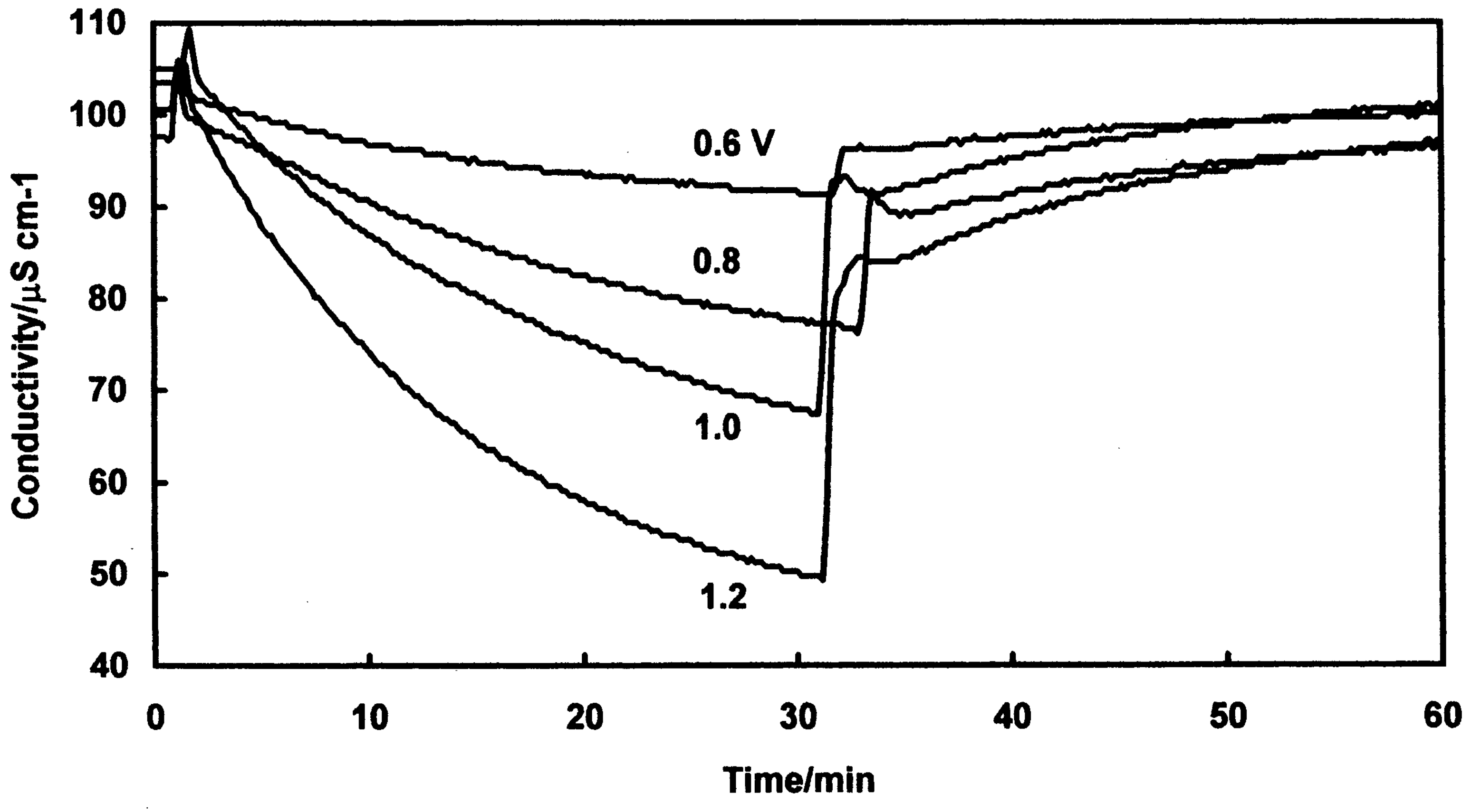

Fig. 3. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 aged electrode pairs operated at voltage differences ranging from 0.6 to 1.2 V.

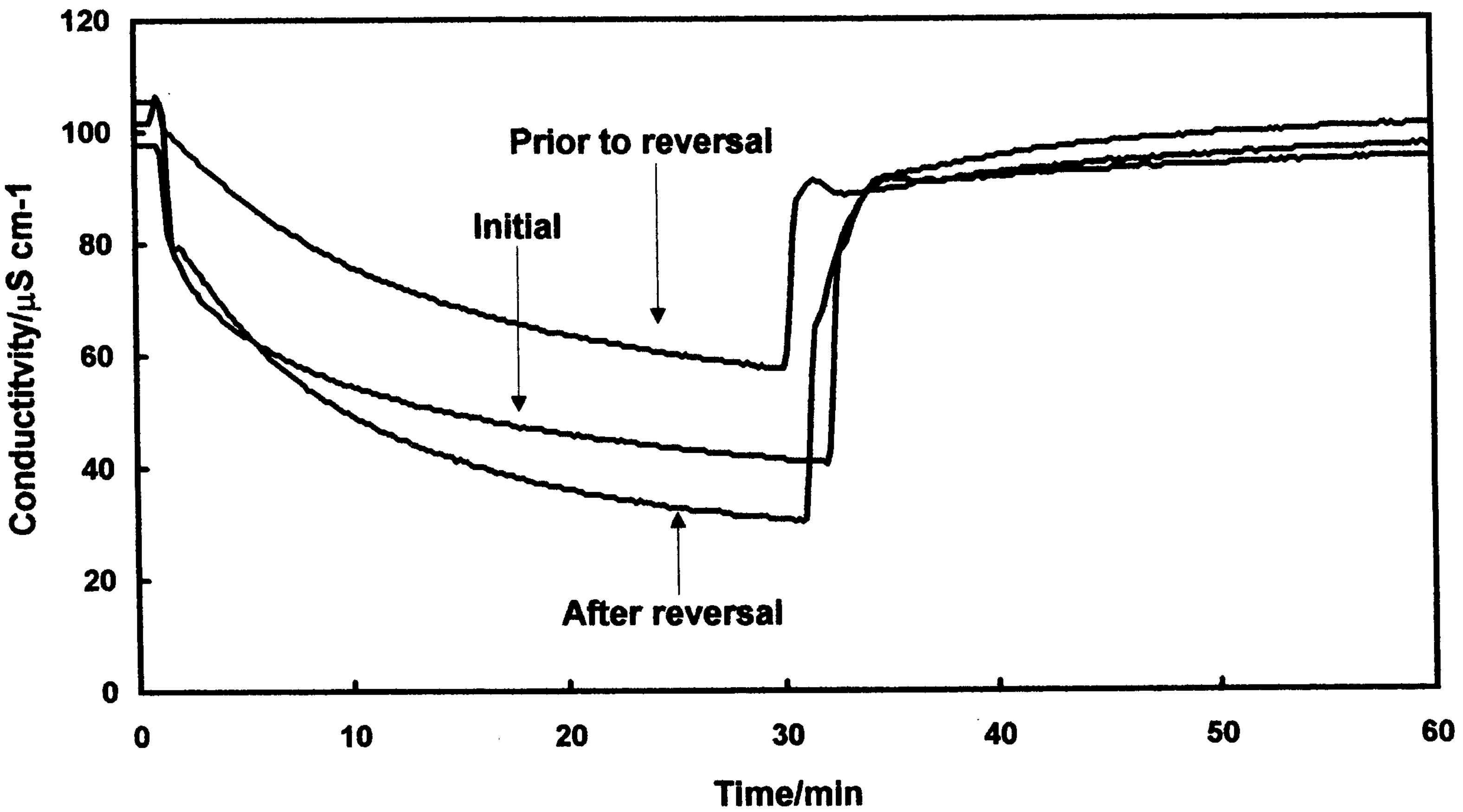

Fig. 4. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 new electrode pairs operated at a cell voltage of 1.2 V.

operation raised the salt removal from approximately 40% to above 70%. 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.

4.3. *Expanded stack with 384 electrode pairs and 100 $\mu S\ cm^{-1}$ solutions*

After a technique for rejuventating the electrodes was developed, a stack with 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 Figs. 5 and 6, a stack of 384 pairs of carbon aerogel electrodes at 1.2 V removes approximately 85% of the NH_4ClO_4 or 95% of the NaCl in a fixed, 4.0 L volume of 100 $\mu S\ cm^{-1}$ solution. Data for the deionization of 100 $\mu S\ cm^{-1}$ NH_4ClO_4 solution at cell voltages of 0.6, 0.8, 1.0, and 1.2 V are compared in Fig. 7. Qualitatively, the results are similar to those for 48 pairs of electrodes. As the concentration of salt in the electrolyte diminishes, the equilibrium surface charge density decreases, as expected. The rejuvenation of 384 pairs of electrodes is illustrated by Fig. 8. The "initial" conductivity transient is before rejuvenation whereas the "after reversal" transients are

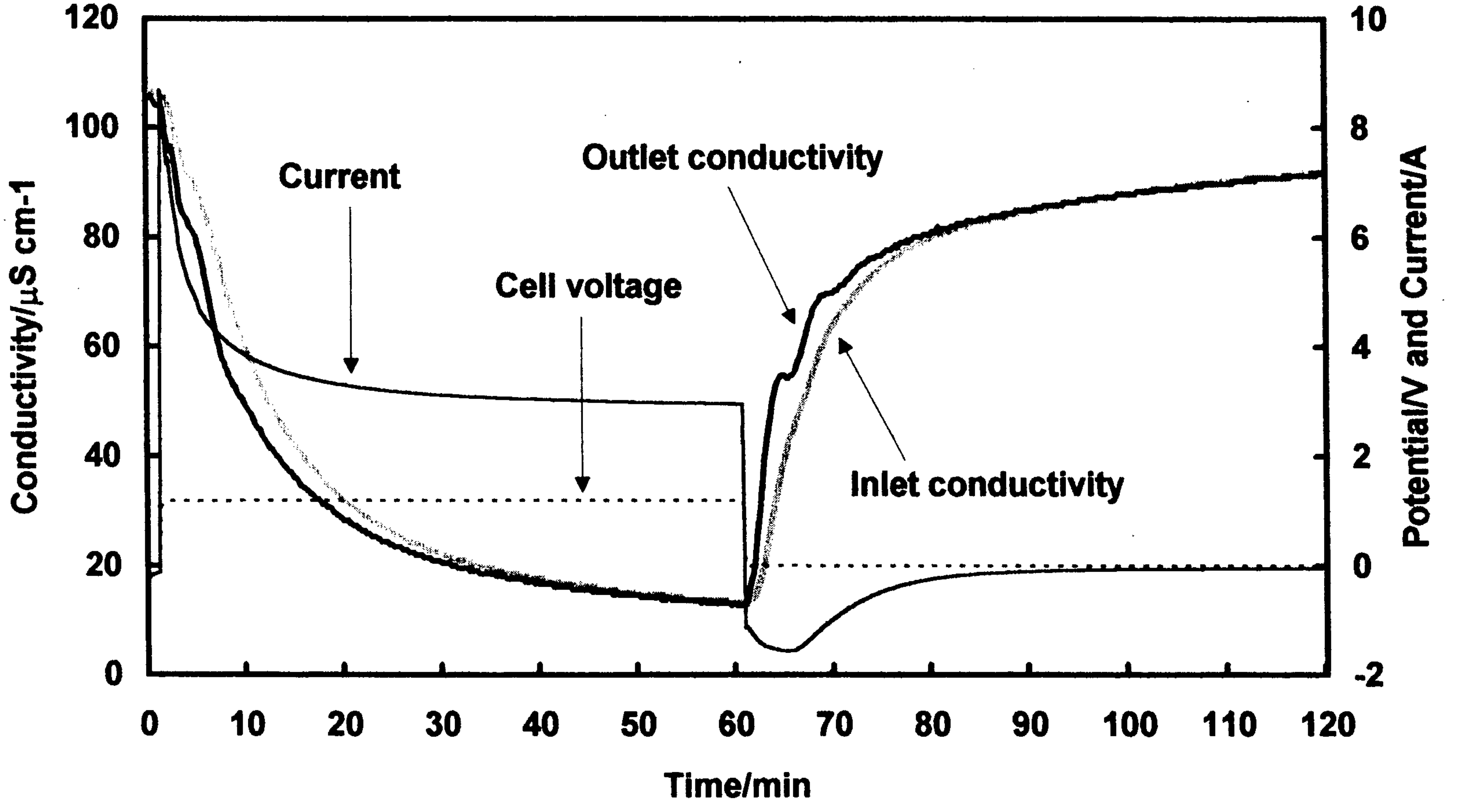

Fig. 5. Deionization of a fixed volume of 100 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

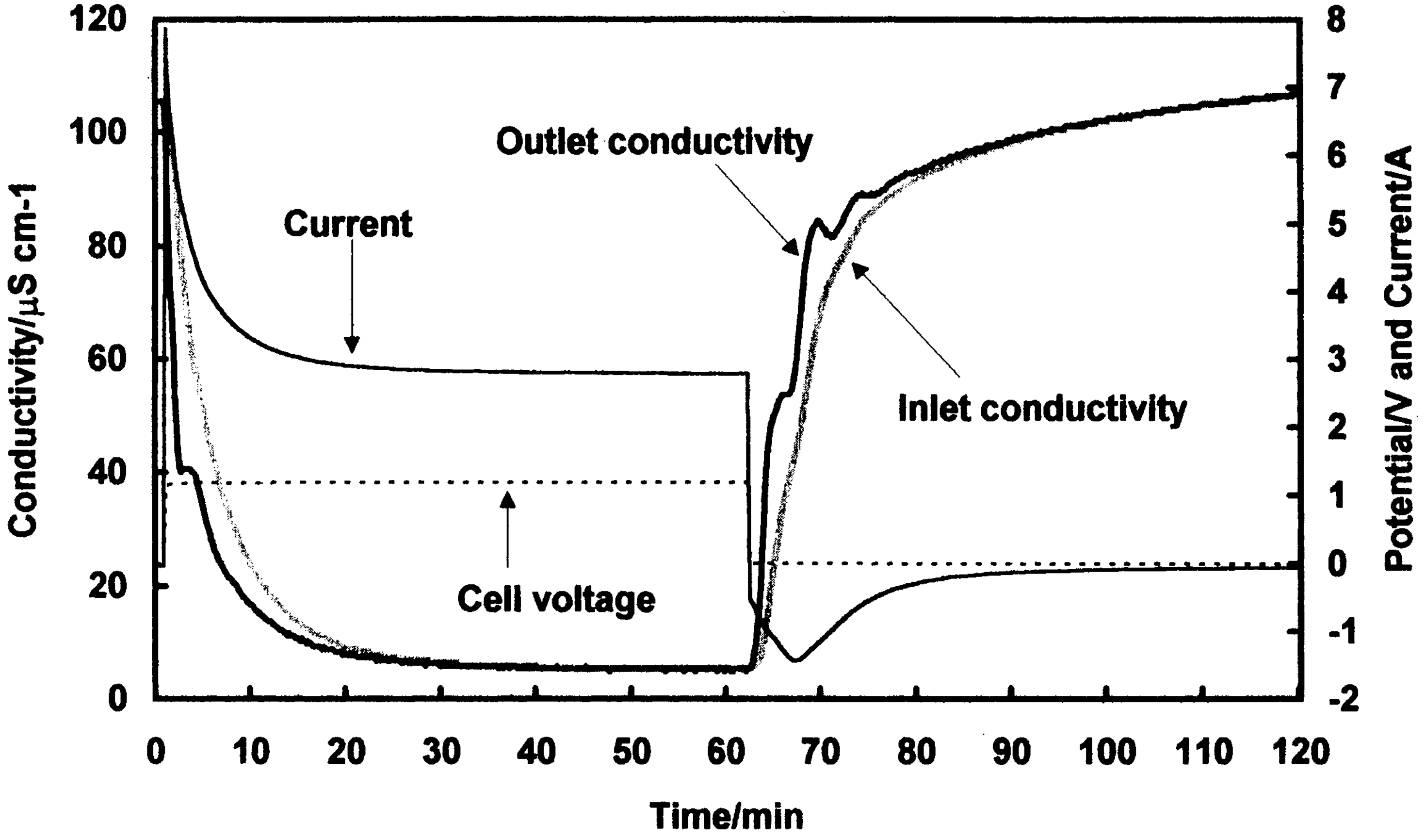

Fig. 6. Deionization of a fixed volume of 100 μS cm^{-1} NaCl solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

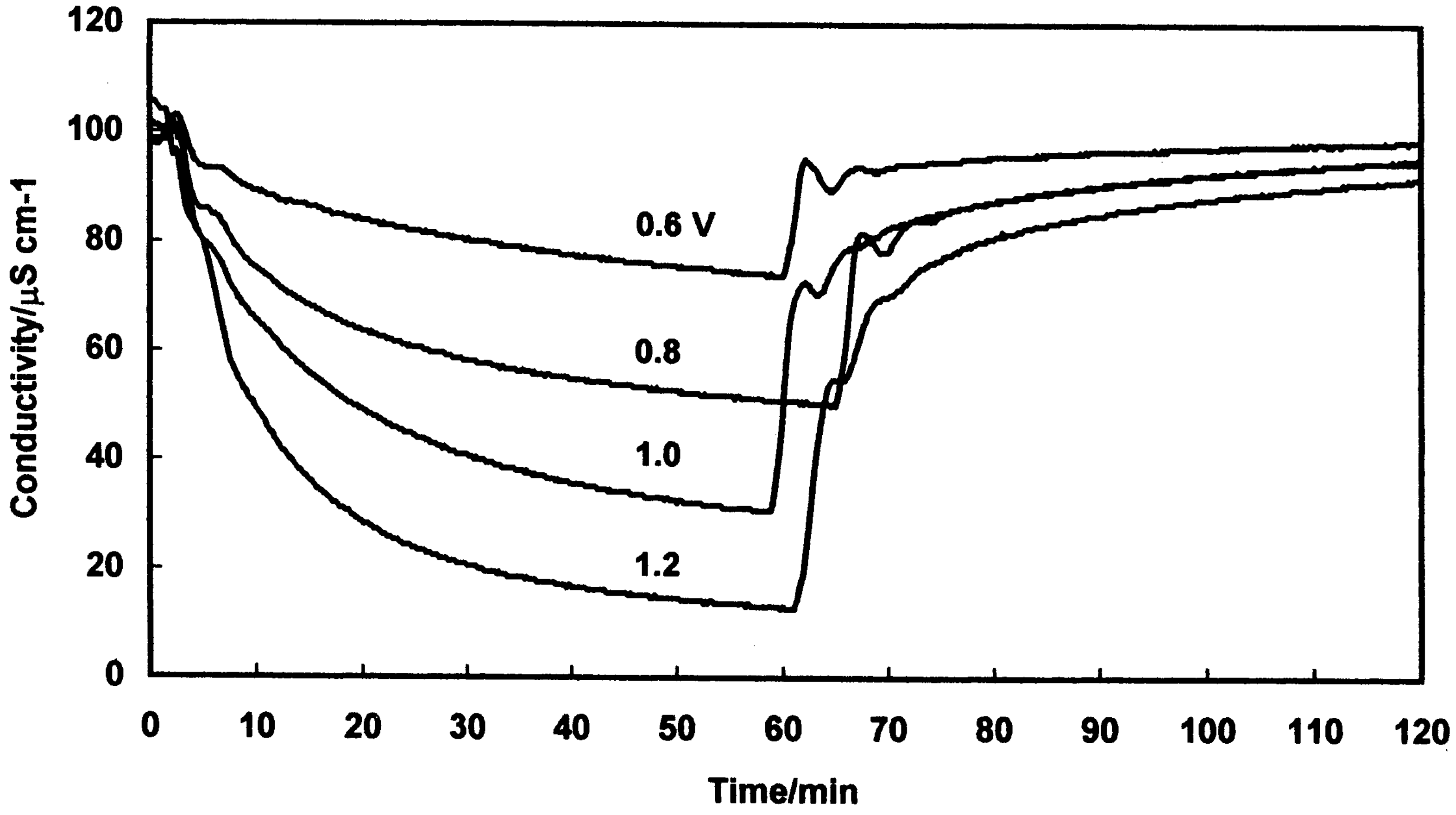

Fig. 7. Deionization of a fixed volume of 100 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

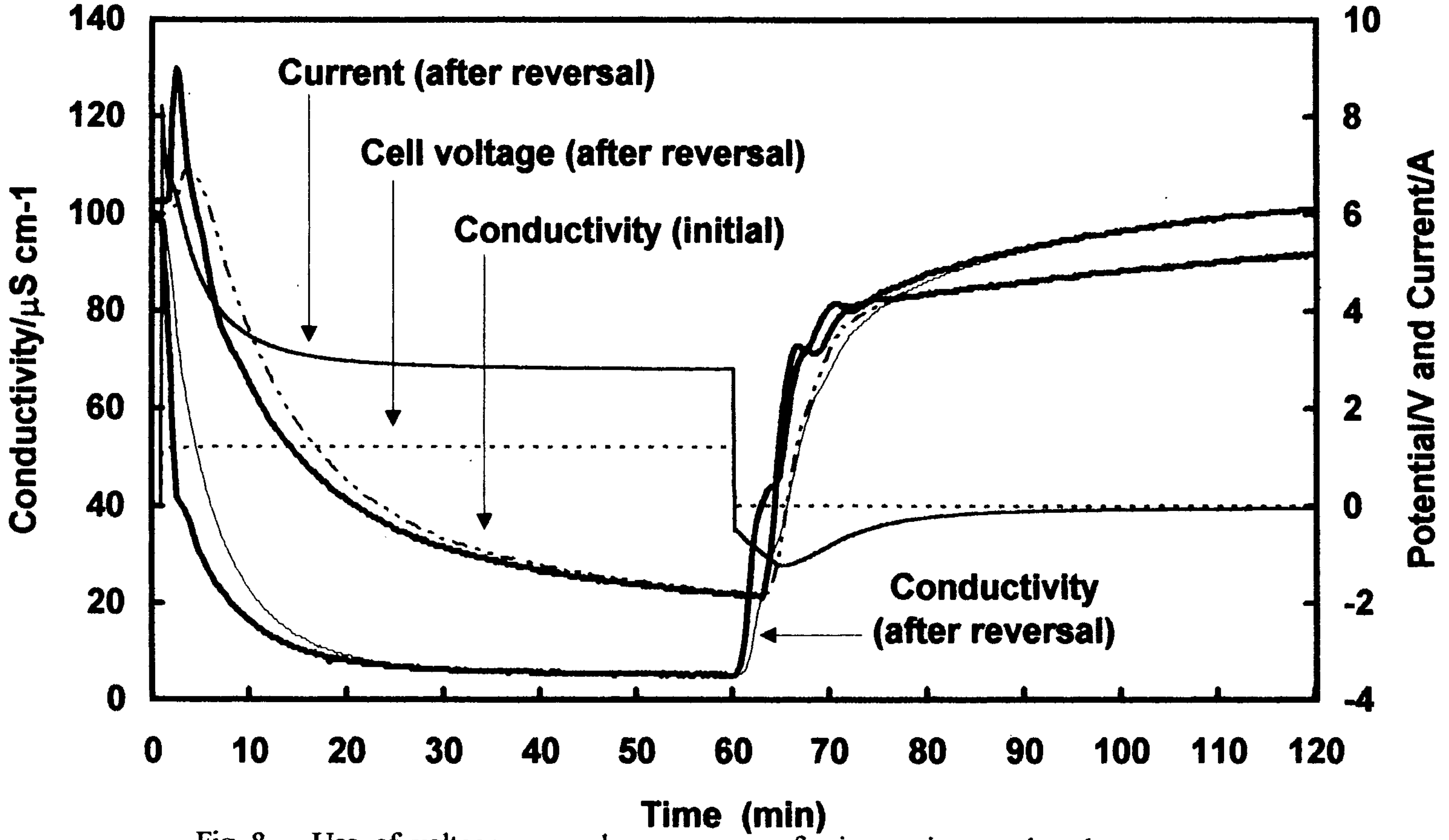

Fig. 8. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

after rejuvenation.

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

Experiments were then conducted with a solution of NH_4ClO_4 that had an initial conductivity slightly greater than 1000 $\mu S\ cm^{-1}$. Voltage, current, and solution conductivity transients during one charge-discharge cycle of such an experiment with aged electrodes at 1.2 V are shown in Fig. 9. 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 concentration 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 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. The effects of electrode aging are apparant in the comparison of the transient for 1.2 V to

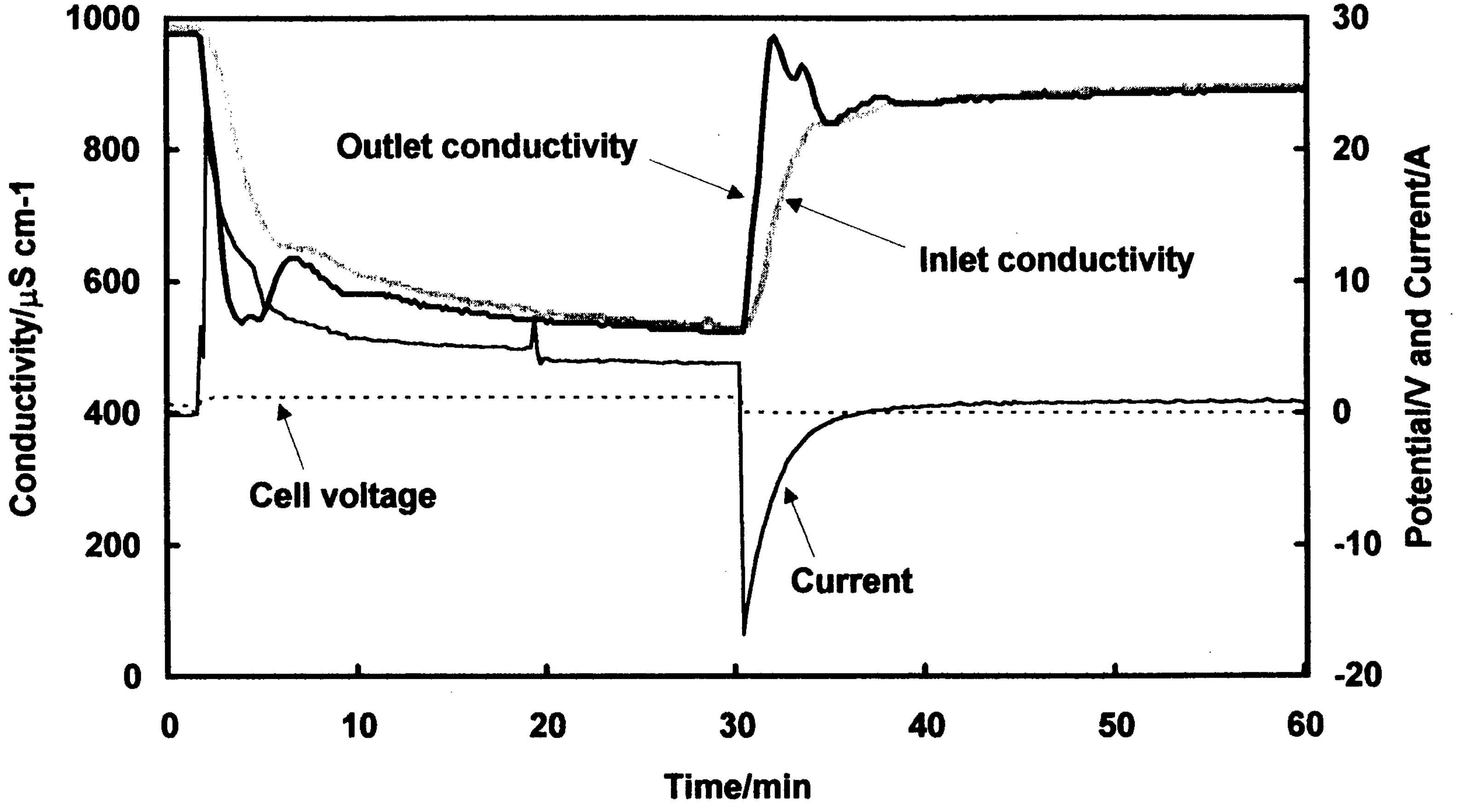

Fig. 9. Deionization of a fixed volume of 1000 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

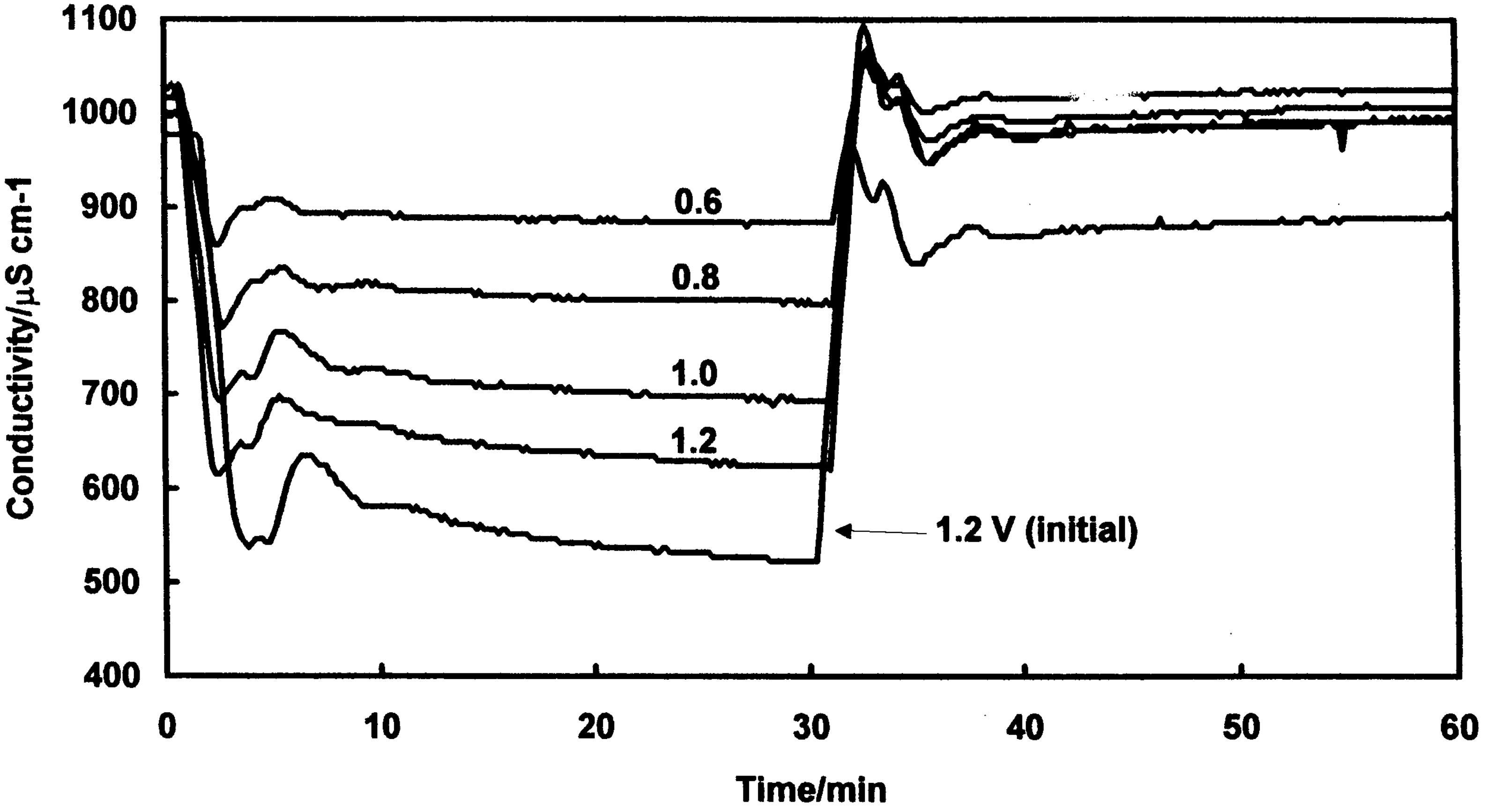

Fig. 10. Deionization of a fixed volume of 1000 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at cell voltages ranging from 0.6 to 1.

one obtained during the initial test with the cell. 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 at 1.2 V has sufficient electrosorption capacity to remove 50% of the salt from a fixed, 4.0 L volume of 1000 μS cm^{-1} NH_4ClO_4 solution.

4.5. *Single-pass experiments with NH_4ClO_4 solutions*

Conductivity transients of a 100 μS cm^{-1} NH_4ClO_4 solutions during single-pass experiments with both 48 and 384 pairs of aged electrodes are shown in Figs. 11 and 12, respectively. The amplitude of the applied voltage was 1.2 V and the flow rate was 25 ml min^{-1}. In the 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. After 120 minutes of operation, the carbon aerogel became saturated (fully charged) with NaCl and breakthrough was observed. The behavior is analogous to that of ion exchange columns. The cell was regenerated by electrical discharge at 150 minutes, at which time the effluent concentration peaked at a level five times (5X) greater than the feed concentration. As expected, the breakthrough

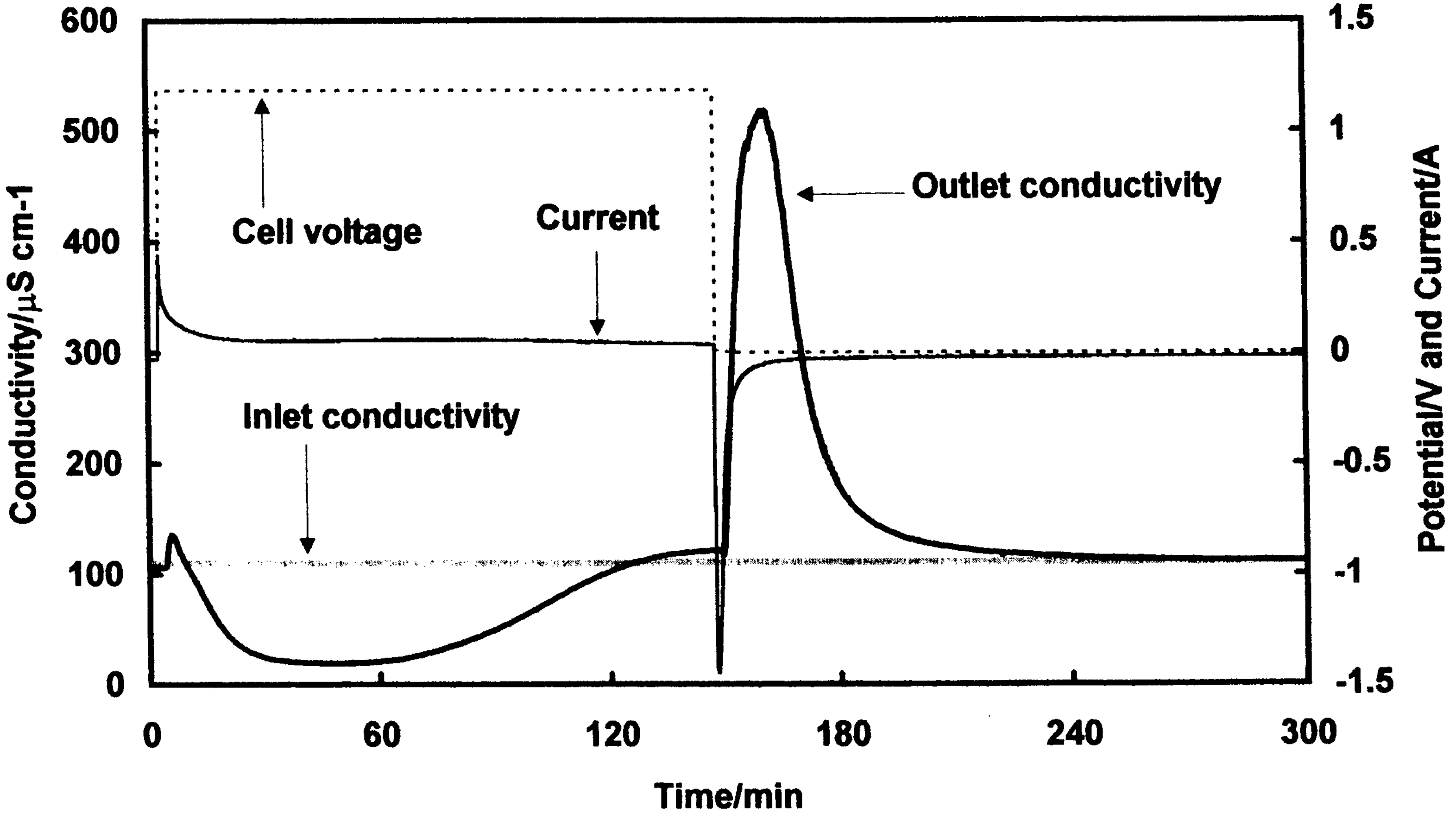

Fig. 11. Single-pass experiment with 100 μS cm^{-1} NH_4ClO_4 solution at a flow rate of 25 ml min^{-1}. The apparatus included 48 electrode pairs operated at cell voltage of 1.2 V.

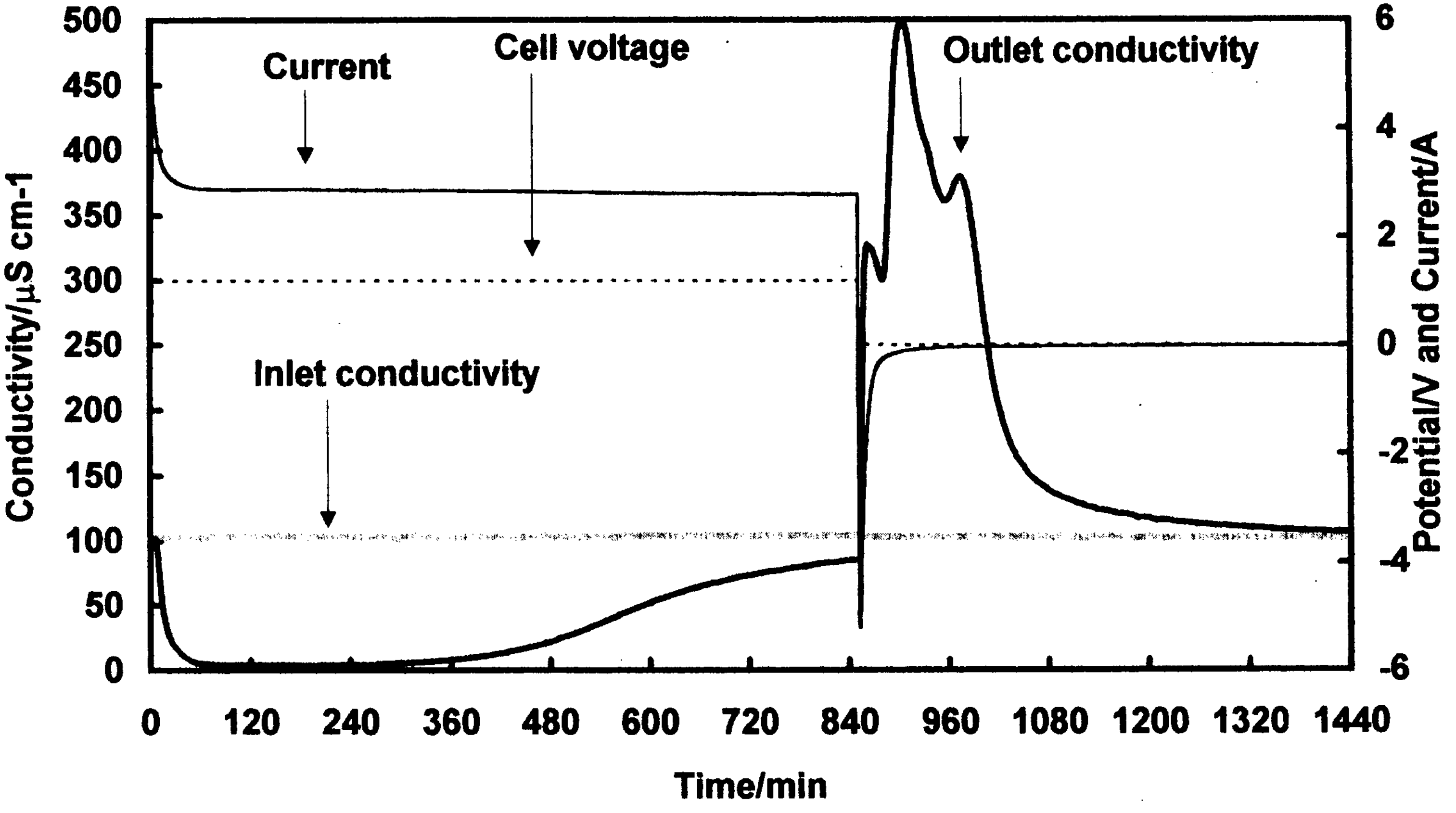

Fig. 12. Single-pass experiment with 100 µS cm^{-1} NH_4ClO_4 solution at a flow rate of 25 ml min^{-1}. The apparatus included 384 electrode pairs operated at cell voltage of 1.2 V.

time was prolonged by increasing the number of electrode pairs from 48 to 384 (Fig. 12). Conductivity transients during similar single-pass experiments with a 1000 μS cm^{-1} NH_4ClO_4 solution and 384 pairs of aged electrodes 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 minutes, representing a salt removal of about 50%. After 60 minutes of operation, the carbon aerogel became saturated (fully charged) with NH_4ClO_4 and breakthrough was observed.

5. 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:

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

where σ is the surface charge density (μC cm^{-2}), C is the electrolyte concentration (mol L^{-1}), 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:

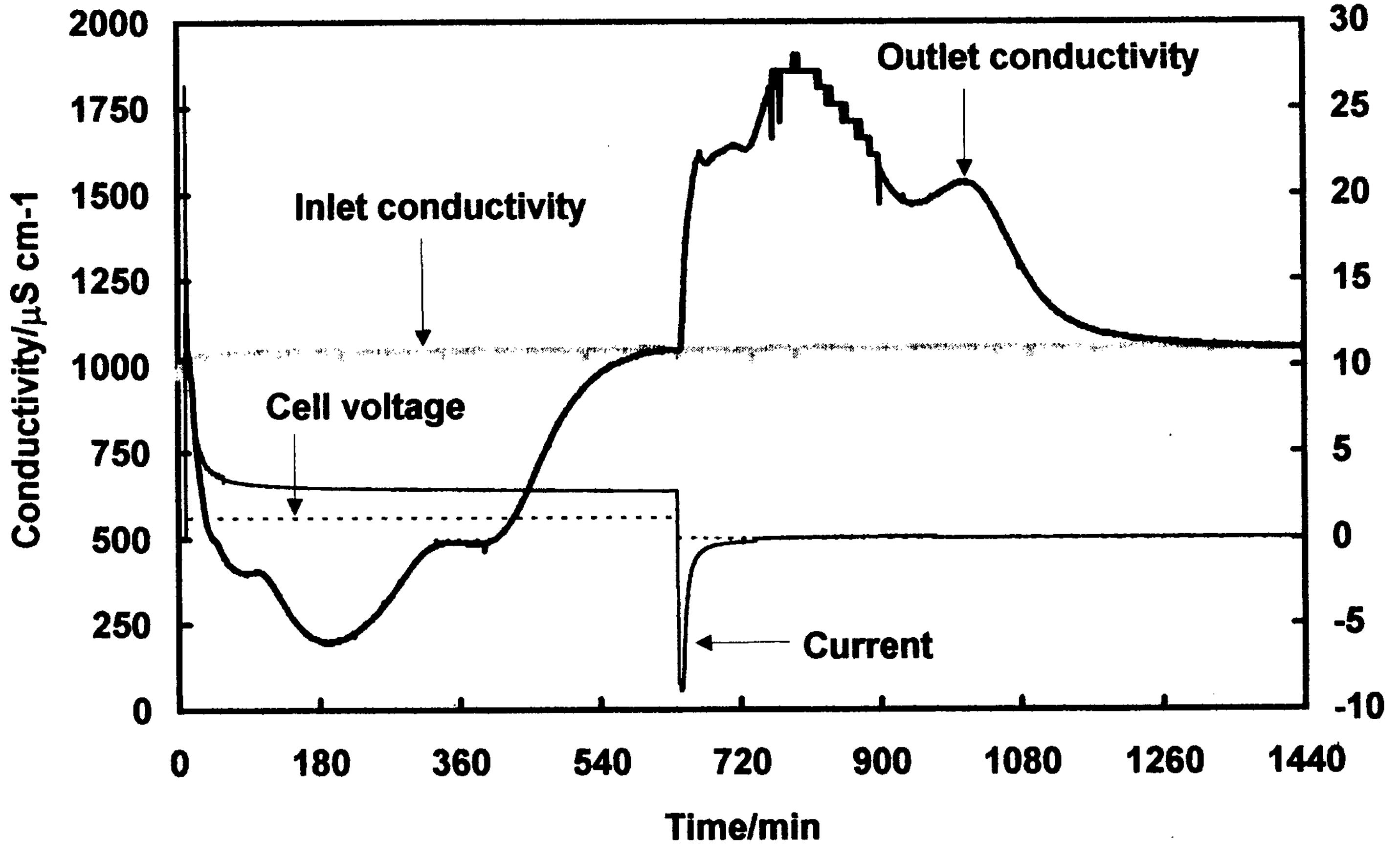

Fig. 13. Single-pass experiment with 1000 µS cm^{-1} NH_4ClO_4 solution at a flow rate of 25 ml min^{-1}. The apparatus included 384 electrode pairs operated at cell voltage of 1.2 V.

$$\sigma \propto C^{0.4} \qquad [2].$$

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.

The electrosorption capacity of a CDI cell built with porous carbon electrodes is limited by its ability to accomodate anions [10]. Typically, the cation capacity is much higher than the corresponding anion capacity. The mass specific chloride capacities for electrodes based on charcoal, carbon black, and graphite are usually below 25 x 10^{-5} equivalents per gram of carbon at NaCl concentrations of 0.03 N. The chloride capacity of carbon aerogel electrodes at 1000 μS cm^{-1} and 1.2 V is approximately 22 x 10^{-5} equivalents per gram of carbon. This value can be extrapolated to 0.03 N by assuming that the surface charge density is proportional to $C^{0.3}$ [34]. The value capacity expected at the higher concenetration is 29 x 10^{-5} equivalents per gram. The approximate perchlorate capacity measured at 1000 μS cm^{-1} with 384 electrodes at 1.2 V is approximately 20 x 10^{-5} equivalents per gram, or 34 x 10^{-5} extrapolated to 0.03 N assuming that surface charge density is proportional to $C^{0.4}$. It appears that anion capacities for carbon aerogel electrodes are as high as any values measured for high surface area activated carbon electrodes. 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 1-3 Ω [10], compared to ~10 μΩ for an aerogel electrode [25]. The value for the aerogel electrode is based on a measured resistivity of 40 mΩ cm. Attempts to make direct measurements of the “through resistance” with a standard digital ohm meter 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 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 N_2 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 at 25°C, the characteristic thickness of the diffuse layer ranges from 1 nm at a concenetration 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 [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 waste water 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 $NaNO_3$ solution contaminated with ^{137}Cs, ^{90}Sr, 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 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 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 a 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, 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 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^{-1} (4.2 Wh gal^{-1}) by the authors, assuming that the NaCl obeys the Debye-Huckel 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 (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.

Additional publications on capacitive deionization with activated carbon composites [34-36] and capacitive deionization with carbon aerogel electrodes have appeared [37-39]. The reader is referred to these works for completeness.

6. 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 concenetrations 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 salt removal for NH_4ClO_4 and NaCl at 1.2 V. Though ClO_4^- and Cl^- 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 times (years). Such 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 sea water 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.

7. Conclusions

The capacitive deionization (CDI) of aqueous solutions of NH_4ClO_4 and NaCl 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, roughly 95% of the NH_4ClO_4 in a 100 $\mu S\ cm^{-1}$ feed stream was removed until saturation of the carbon aerogel electrodes was reached. 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. 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.

8. Acknowledgments

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 U.S. Department of Energy (DOE) by Lawrence Livermore National Laboratory (LLNL) under Contract No. W-7405-Eng-48.

9. References

[1] J. A. Trainham, J. Newman, "Flow-Through Porous Electrode Model: Application to Metal-Ion Removal from Dilute Streams," J. Electrochem. Soc. 124 10 (1977) 1528-1540.

[2] Van Zee, J. Newman, "Electrochemical Removal of Silver Ions from Photographic Fixing Solutions Using a Porous Flow-Through Electrode," J. Electrochem. Soc. 124 5 (1977) 706-708.

[3] K. Moeglich, "Apparatus for Removal of Contaminants from Water," U.S. Pat. No. 4,072,596, February 07, 1978.

[4] W. J. Blaedel, J. C. Wang, "Flow Electrolysis on a Reticulated Vitreous Carbon Electrode," Anal. Chem. 51 7 (1979) 799-802.

[5] T. Risch, J. Newman, "Flow-Through and Flow-By Porous Electrodes at the Limiting Current," J. Electrochem. Soc. 131 11 (1984) 2551-2556.

[6] P. Lessner, J. Newman, "Hydrodynamics and Mass Transfer in a Porous-Wall Channel," J. Electrochem. Soc. 131 8 (1984) 1828-1831.

[7] G. F. Platek, "Reticulated Electrode for Recovery of Metal Ions," U.S. Pat. No. 4,515,672, May 07, 1985.

[8] M. Matlosz, J. Newman, "Experimental Investigation of a Porous Carbon Electrode for the Removal of Mercury from Contaminated

Brine," J. Electrochem. Soc., 133 9 (1986) 1850-1859.

[9] B. B. Arnold, G. W. Murphy, "Studies on the Electrochemistry of Carbon and Chemically Modified Carbon Surfaces," J. Phys. Chem. 65 1 (1961) 135-138.

[10] D. D. Caudle, J. H. Tucker, J. L. Cooper, B. B. Arnold, A. Papastamataki, "Electrochemical Demineralization of Water with Carbon Electrodes," Research and Development Progress Report No. 188, United States Department of Interior, May 1966, 190 p.

[11] A. M. Johnson, A. W. Venolia, J. Newman, R. G. Wilbourne, C. M. Wong, , W. S. Gillam, S. Johnson, R. H. Horowitz, "Electrosorb Process for Desalting Water," Office of Saline Water Research and Development Progress Report No. 516, U.S. Dept. Interior Pub. 200 056, March 1970, 31 p.

[12] A. M. Johnson, A. W. Venolia, R. G. Wilbourne, J. Newman, "The Electrosorb Process for Desalting Water," Marquardt Co., Van Nuys, CA, March 1970, 36 p.

[13] A. M. Johnson, "Electric Demineralizing Apparatus," U.S. Pat. No. 3,515,664, June 2, 1970.

[14] A. M. Johnson, J. Newman, "Desalting by Means of Porous Carbon Electrodes," J. Electrochem. Soc., 118 3 (1971) 510-517.

[15] Y. Oren, A. Soffer, "Electrochemical Parametric Pumping," J.

Electrochem. Soc. 125 6 (1978) 869-875.

[16] Y. Oren, A. Soffer, "Water Desalting by Means of Electrochemical Parametric Pumping: I. The Equilibrium Properties of a Batch Unit Cell," J. Appl. Electrochem. 13 4 (1983) 473-487.

[17] Y. Oren, A. Soffer, "Water Desalting by Means of Electrochemical Parametric Pumping: II. Separation Properties of a Multistage Column," J. Appl. Electrochem. 13 4 (1983) 489-505.

[18] Keitaro Katsu, "Double Layer Electric Capacitor," Nippon Electric Co., Jap. Pat. Appl. 91-303689.

[19] "Electric Double-layer Capacitor," Matsushita Electric Industrial Co., Ltd., Jap. Pat. Appl. 83-89451.

[20] J. Tabuchi, Y. Kibi, T. Saito, 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 Electrochem. Soc. Mtg., Honolulu, HI, May 16-21, 1993.

[21] "Electrical Double-layer Capacitor, Uses Porous Polarized Electrode Consisting of Carbonized Foamed Phenol Resin," Mitsui Petrochem Ind., Jap. Pat. Appl. 89-210642.

[22] S. T. Mayer, R. W. Pekala, J. L. Kaschmitter, "The Aerocapacitor: An Electrochemical Double-layer Energy-Storage Device," J.

Electrochemical Society 140 2 (1993) 446-451.

[23] F. M. Delnick, D. Ingersoll, D. Firsich, "Double-layer Capacitance of Carbon Foam Electrodes," SAND-93-2681, Sandia National Laboratory, Albuquerque, NM, 1993, 10 p.

[24] B. Wessling, H. Volk, M. Hilleberg, C. Funder, O. Siemers, H. Merkle, "Stable Electrode for Electrolytic Process (Desalination and Drying) Contains Thermoplastic Polymer and Material Giving Conductivity and Stable Potential," U.S. Pat. No. 4,806,212.

[25] R. W. Pekala, S. T. Mayer, J. F. Poco, J. L. Kaschmitter, "Structure and Performance of Carbon Aerogel Electrodes," in Novel Forms of Carbon II, C. L. Renschler, D. M. Cox, J. J. Pouch, Y. Achiba, Eds., MRS Symp. Proc. 349 79 (1994).

[26] D. O. Campbell, E. D. Collins, L. J. King, J. B. Knauer, "Process improvement studies for the Submerged Demineralizer System (SDS) at the Three Mile Island Nuclear Power Station, Unit 2," ORNL/TM-7756, Oak Ridge National Laboratory, Oak Ridge, TN, May 1982, 30 p.

[27] J. Wang et al., "Carbon Aerogel Composite Electrodes," Anal. Chem. 65 (1993) 2300-2303.

[28] R. W. Pekala et al., "Supercapacitors Based on Carbon Foams," U.S. Pat. No. 5,260,855.

[29] R. W. Pekala, C. T. Alviso, in Novel Forms of Carbon, C. L. Renschler, J. J. Pouch, D. M. Cox, Eds., MRS Symp. Proc. 270 3 (1992).

[30] R. W. Pekala, in Ultrastructure Processing of Advanced Materials, D. R. Uhlmanjn, D. R. Ulrich, Eds., John Wiley and Sons, Inc., New York, NY, 1992, pp. 711-717.

[31] A. J. Bard, L. R. Faulkner, Electrochemical Methods, Fundamentals and Applications, John Wiley and Sons, New York, NY, 1980, pp. 500-515.

[32] C. J. King, Separation Processes, 2nd Ed., McGraw-Hill, San Francisco, CA, 1980, pp. 661-664.

[33] J. S. Newman, Electrochemical Systems, 2nd Ed., Prentice Hall, Englewood Cliffs, NJ, 1991, pp. 89-94.

[34] M. D. Andelman, "Flow-Through Capacitor," U.S. Pat. No. 5,415,768, May 16, 1995.

[35] M. D. Andelman, "Chromatography System," U.S. Pat. No. 5,360,540, November 1, 1994.

[36] T. Otowa, "A Planar, Flow-Through, Electric Double-Layer Capacitor and Method of Treating Fluids with the Capacitor," International Patent Application Number PCT/US94/05364, November 24, 1994.

[37] J. C. Farmer, "Method and Apparatus for Capacitive Deionization,

Electrochemical Purification, and Regeneration of Electrodes," U.S. Pat. No. 5,425,858, June 20, 1995.

[38] J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala, J. F. Poco, "Capacitive Deionization of Water: An Innovative New Process," Proceedings of the Fifth International Conference on Radioactive Waste Management and Environmental Remediation, Berlin, Germany, September 3-9, 1995, American Society of Mechanical Engineers (ASME), New York, NY, Vol. 2, pp. 1215-1220, 1995.

[39] J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala, J. F. Poco, "Capacitive Deionization of NaCl and NaNO3 Solutions with Carbon Aerogel Electrodes," Rept. UCRL-JC-120349, Lawrence Livermore National Laboratory, Livermore, CA (1995); J. Electrochem. Soc., in press.

Figure Captions

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

Fig. 2. Deionization of a fixed volume of 100 μS cm^{-1} NaCl solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 aged electrode pairs operated at a cell voltage of 1.2 V.

Fig. 3. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 aged electrode pairs operated at voltage differences ranging from 0.6 to 1.2 V.

Fig. 4. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 2.0 L at a rate of 1.0 L min^{-1}. The apparatus included 48 new electrode pairs operated at a cell voltage of 1.2 V.

Fig. 5. Deionization of a fixed volume of 100 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

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

Fig. 7. Deionization of a fixed volume of 100 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

Fig. 8. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 µS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

Fig. 9. Deionization of a fixed volume of 1000 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

Fig. 10. Deionization of a fixed volume of 1000 μS cm^{-1} NH_4ClO_4 solution. Complete recycle of 4.0 L at a rate of 1.0 L min^{-1}. The apparatus included 384 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.

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.