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Production and Use of Carbon-Based Materials for Environmental Cleanup
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THE USE OF CARBON AEROGEL ELECTRODES FOR ENVIRONMENTAL CLEANUP

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Keywords: carbon aerogel electrodes, deionization of water, heavy metal removal from water

ABSTRACT

Carbon aerogel has a very high specific surface area (400 to $1100 \text{ m}^2 \text{ g}^{-1}$), a relatively large pore size ($\sim 50 \text{ nm}$), and exceptionally low electrical resistivity ($\leq 40 \text{ m}\Omega\text{-cm}$). Such properties make this monolithic material ideal for some electrode applications. An electrochemical cell with a stack of carbon aerogel electrodes has been constructed and used to remove a variety of contaminants from aqueous waste streams and natural waters. In the case of non-reducible and non-oxidizable salt solutions, the cell is operated in a capacitive mode. Electrolytic or electrophoretic deposition is used for the removal of heavy metals. It has been shown that capacitive deionization with carbon aerogel electrodes can be used to remove salts such as NaNO_3 from water. It has also shown that electrolysis with carbon aerogel electrodes can be used to effectively remove a variety of heavy metals from process streams and natural waters. The exceptional electrical conductivity carbon aerogel is due to its unique interconnected nanostructure and has made it possible to eliminate the need for metal substrates in more recent cell designs.

ACKNOWLEDGMENT

Funding for the development of the electrochemical cell with the carbon aerogel electrodes was provided by the Strategic Environmental Research and Development (SERDP) Program, under the direction of Dr. John Harrison. Funding for the treatability studies was provided by the Environmental Compliance Division of Armstrong Laboratory, Tyndall Air Force Base. These studies were directed by Lt. Ray Anthony Smith. 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.

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INTRODUCTION

An electrochemical cell with a stack of carbon aerogel electrodes has been used to remove a variety of contaminants from aqueous waste streams and natural waters. In the case of non-reducible and non-oxidizable salt solutions, the cell is operated in a capacitive mode [1-7]. Electrolytic or electrophoretic deposition is used for the removal of heavy metals. The removal of NaNO_3 from water with subsequent concentration is an example of capacitive operation. Electrodialysis with bipolar membranes can be used to separate neutral salt solutions into their acid and base components so that recycle is possible, thereby lowering risk to the environment [8]. However, the electrodialysis process is not 100% efficient and generates a dilute waste stream of NaNO_3 in addition to the HNO_3 and NaOH product streams. Carbon aerogel electrodes can be used to remove NaNO_3 from the effluent, concentrating it for recycle to the electrodialysis cell. Solutions are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to $1100 \text{ m}^2 \text{ g}^{-1}$) and very low electrical resistivity (less than $40 \text{ m}\Omega\text{-cm}$). After polarization, Na^+ cations and NO_3^- anions are removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes. Two streams are produced, pure water and NaNO_3 concentrate. This process is also capable of removing other impurities such as dissolved heavy metals and suspended colloids. In these cases, contaminants are removed by electrodeposition and electrophoresis, respectively. The carbon aerogel cell has been used for the separation of copper, zinc, cadmium, and lead from 0.1 M KNO_3 solutions, as well as for the separation of cobalt, chromium, manganese, lead, and uranium from sea water. Treatability tests on ground water at LLNL have shown that chromium contamination can be reduced from 32 to 2 ppb, well below the acceptable level of 11 ppb. Previously, other types of porous carbon electrodes have been used for the removal of heavy metals from water. These electrolytic separation processes have 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 either electrical discharge or reverse polarization. Therefore, no secondary waste is generated. In contrast to thermal processes such as evaporation, such processes are more energy efficient. Since no high pressure pumps are required, these electrolytic separation processes offer operational advantages over reverse osmosis (RO).

ELECTROCHEMICAL CELL WITH CARBON AEROGEL ELECTRODES

A typical double-sided electrode is 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 silver epoxy is used for gluing. Carbon aerogels were developed at Lawrence Livermore National Laboratory and are synthesized by the polycondensation of resorcinol and formaldehyde in a slightly basic medium, followed by supercritical drying and pyrolysis in an inert atmosphere. Sheets of CAC are made by impregnating carbon cloth with the resorcinol-formaldehyde solution and then carbonizing. This fabrication process results in unique open-cell carbon foams that have high specific surface areas (400 to $1100 \text{ m}^2 \text{ g}^{-1}$), optimal pore sizes ($\sim 50 \text{ nm}$), and a monolithic structure composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of 10 nm . This structure results in exceptionally low electrical resistivity ($40 \text{ m}\Omega\text{-cm}$). 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. Each sheet of CAC used in the experiments described here is $6.86 \text{ cm} \times 6.86 \text{ cm} \times 0.0125 \text{ cm}$, has a total active surface of approximately $2.8 \times 10^6 \text{ cm}^2$, and a through resistance of about $10 \mu\Omega$. 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. 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. Flow through the cell is generated by a programmable, magnetically-coupled, screw pump with a 304 stainless steel head. The maximum flow rate that can be achieved with this pump is 3.5 L/min. The differential pressure across a stack of 48 electrodes is only 5 psi at a flow rate of 1.7 L/min. All lines are made of Teflon and have a nominal diameter of 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 cell. 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. 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. X-ray fluorescence is used off line for the quantitative measurement of heavy metals.

REMOVAL OF NITRATE SALTS

The removal NaNO_3 from a fixed 4000 ml volume of water by a stack of 192 carbon aerogel electrodes is illustrated by Fig. 1. The circulation rate through the stack was approximately 1000 ml/min. After application of a voltage between two adjacent electrodes, Na^+ cations and NO_3^- 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. Tests demonstrated that CDI with carbon aerogel can effectively remove NaNO_3 from water. Deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentration and conductivity was cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, i.e., the electrosorption capacity, had a strong dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.6 V. During experiments without recycle, a characteristic breakthrough curve (not shown) was observed. Deionization of more concentrated solutions requires more carbon aerogel electrodes.

REMOVAL OF HEAVY METALS

Two carbon aerogel electrodes polarized at 1.2 V can remove copper, zinc, cadmium, and lead from a fixed, 500 ml volume of a 0.1 M KNO_3 solution (Fig. 2). The electrolyte was circulated through the electrochemical cell at a rate of 50 ml/min. The concentration of lead dropped from an initial level of approximately 1 ppm to less than 0.2 ppm after 4 hours of polarization. The concentration of copper dropped from 1 ppm to less than 0.05 ppm. At such low concentrations, one would expect rates of removal to be mass transfer controlled, similar in magnitude, and independent of the standard electrode potentials of the ions being deposited. However, the rates for several of the ions appear to be correlated to some extent with their standard electrode potentials, indicating that process efficiency may not be governed by mass transport alone. Forty carbon aerogel electrodes polarized at 1.2 V were able to remove trace quantities of cobalt, chromium, manganese, lead, and uranium from a fixed, 1000 ml volume of sea water (Fig. 3). Here too the electrolyte was circulated through the electrochemical cell at a rate of 50 ml/min. The initial concentration of each contaminant was 100 ppb. After 5 hours of polarization, the concentrations of cobalt, chromium, manganese, and uranium dropped to levels of about 5 ppb or less. The concentration of lead dropped to about 15 ppb. The slow increases in concentration observed between 5 and 25 hours are probably due to some combination of redissolution and particle entrainment. Such difficulties can be avoided by periodic regeneration of the carbon aerogel electrodes. No electrode separator was used in the experiments represented by Figs. 2 and 3. By incorporating an anion exchange membrane between anodes and cathodes, electrode regeneration by stripping is possible.

SUMMARY

In summary, it has been shown that capacitive deionization with carbon aerogel electrodes can be used to remove salts such as NaNO_3 from water. It has also been shown that electrolysis with carbon aerogel electrodes can be used to effectively remove a variety of heavy metals from process streams and natural waters. The exceptionally low electrical resistivity of the monolithic carbon aerogel electrodes, due to their unique interconnected nanostructure, has made it possible to eliminate metal substrates such as titanium in more recent cell designs. Recent cell designs use only carbon aerogel and a plastic such as polycarbonate. Disposable cells made of carbon aerogel and plastic are now being made and operated.

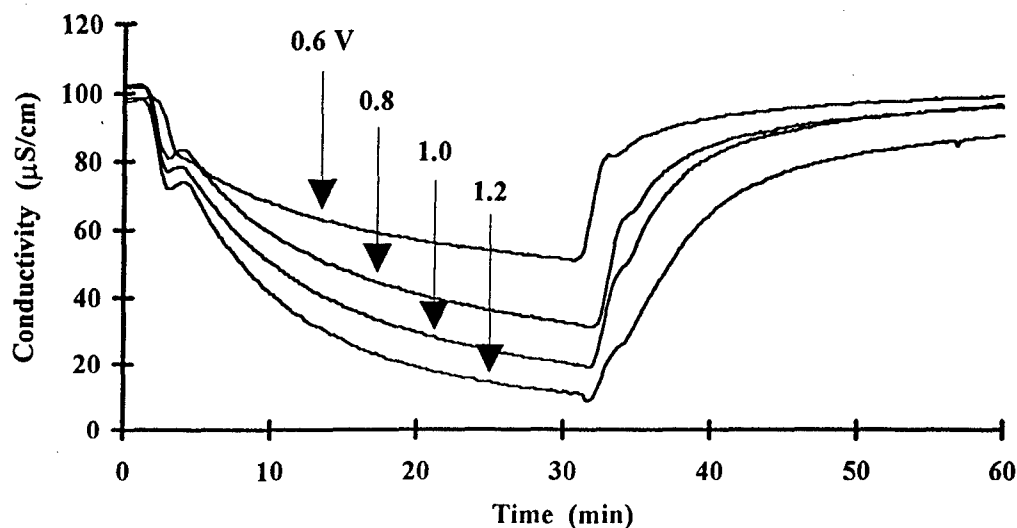


Fig. 1. Use of carbon aerogel electrodes in capacitive mode to remove NaNO_3 from fixed volume of electrolyte.

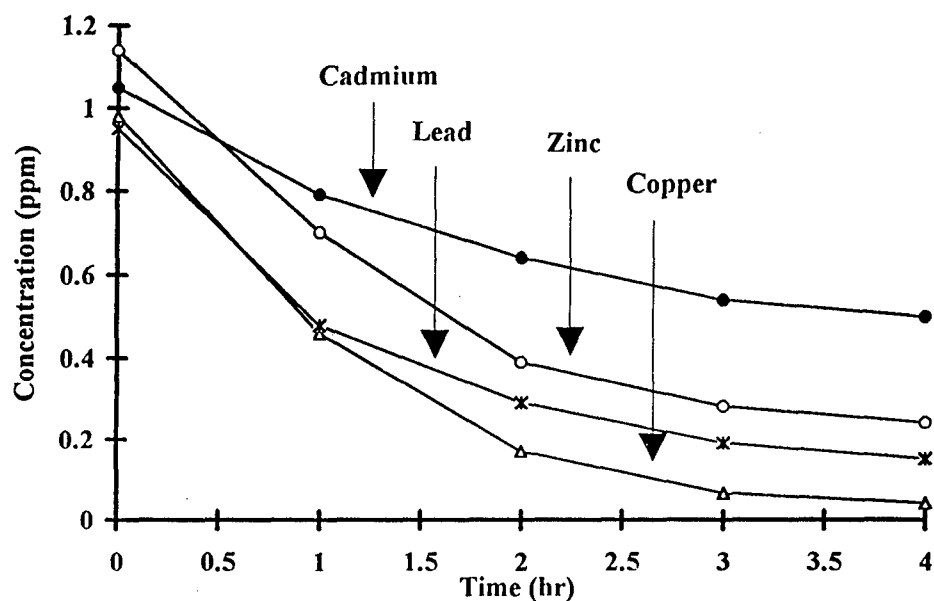


Fig. 2. Use of two carbon aerogel electrodes polarized at 1.2 V to remove copper, zinc, cadmium, and lead from a fixed 500 ml volume of a 0.1 M KNO_3 solution.

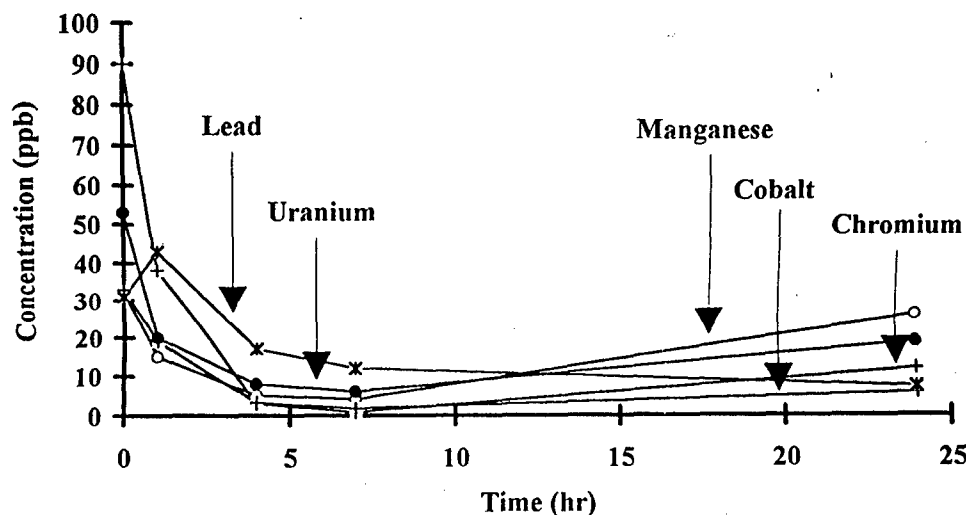


Fig. 3. Use of forty carbon aerogel electrodes polarized at 1.2 V to remove cobalt, chromium, manganese, lead, and uranium from fixed 1000 ml volume of sea water.

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