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Abstract: Capacitive deionization is a new technology being developed for the purification of ocean and brackish well water. A constant voltage is applied and soluble salts are collected on the surface of porous carbon electrodes, thus purifying the water for human consumption or industrial processes. Unfortunately, the current carbon aerogel electrodes are very expensive and their ion storage capacity is relatively low. The main problem is that the cost of the electrodes is too high due the high cost of the resorcinol from which the electrodes are made.

At TDA we have developed a route to monolithic carbon electrodes with a combination of large (mesopores) and small pores (micropores) that is much easier and much less expensive to make than carbon aerogel electrodes. The benefit of the mesopores is that they allow the liquid to penetrate the carbon for easy access to the high surface area micropores. This greatly increases the rate of salt uptake and the useful capacity of the electrodes. In Phase I we developed monolithic porous carbon electrodes with the correct pore size distribution for use in capacitive deionization from low-cost precursors. In Phase II the electrodes will be further optimized, production will be scaled up, and the carbon electrodes will be tested in commercial capacitive deionization systems.

1 Introduction

Obtaining a reliable and plentiful supply of clean water is becoming much more difficult. The arid regions of the Western United States are already depleting their groundwater supplies because surface water rights are completely committed, and the population of the affected area is expected to double in the next twenty-five years. The Middle East and Africa are currently experiencing serious shortages of potable water, and population growth are rapidly making the problem more serious. There are large reserves of brackish (saline) water that could be used to ease these supply problems; if there was a way to cost effectively desalinate them.

Capacitive deionization technology (CDT) is an exciting new method of desalinating brackish water. In CDT, a brackish water stream flows between pairs of high surface area carbon electrodes that are held at a potential difference of 1.2 V. The ions and other charged particles (such as microorganisms) are attracted to and held on the electrode of opposite charge. The negative electrode attracts positively charged ions (cations) such as calcium (Ca), magnesium (Mg) and sodium (Na), while the positively charged electrode attracts negative ions (anions) such as chloride (Cl) and nitrate (NO₃) (Figure 1).

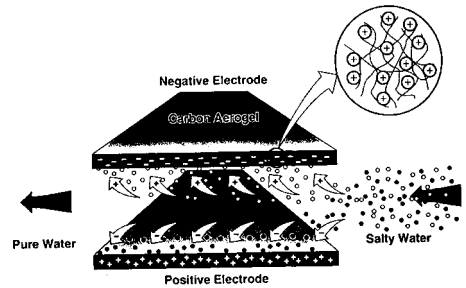


Figure 1 Principal of operation of CDT (during the active desalination half cycle) (Farmer et al. 1996).

Eventually the electrodes become saturated with ions and must be regenerated. The applied potential is removed, and since there is no longer any reason for the ions to remain attached to the electrodes the ions are released and flushed from the system, producing a more concentrated brine stream.

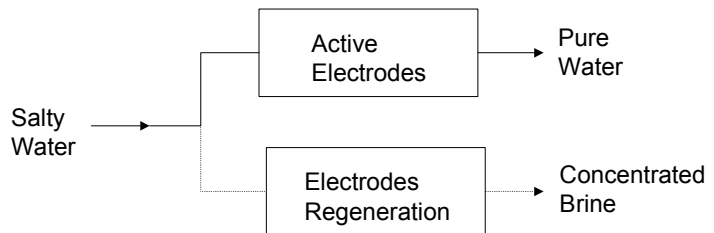


Figure 2. Overall schematic of a CDT system.

In practice, for a gallon of water fed to the a CDT process, more than 80% emerges as fresh, deionized potable water, and the remainder is discharged as a concentrated brine solution containing virtually all of the salts in the feed (Figure 2). The primary advantage of CDT is its low operating cost, which is about one third that of the main competitor, reverse osmosis (RO). This is important because operating costs dominate the cost of desalination.

The leading developer of capacitive deionization systems is CDT Systems, Inc. (Dallas, TX). CDT Systems is solely dedicated to the commercialization of CDT, has its first demonstration plant up and running in Carlsbad, CA, and has signed contracts to supply systems to Arizona Public Service to purify industrial water and the Kingdom of Jordan to purify municipal water. They have established alliances with Asea Brown Boveri (ABB, Norwalk, CT), the \$31 billion power generation, chemical and industrial constructor and services company and Air Water, Inc. (Osaka, Japan), a \$1.8 billion environmental equipment and services company. CDT Systems is our partner in this Phase II project.

CDT Systems has licensed the original Lawrence Livermore National Laboratory patent on CDT (Farmer, 1995), as well as several Livermore patents on methods for making the electrodes; CDT was invented at Livermore in the early 1990s. The Livermore method for making electrodes was an outgrowth of Pekala's pioneering work on carbon aerogels from resorcinol formaldehyde (RF) resins (Pekala 1992, 1994). The basic method consists of impregnating a carbon paper support with a water-resorcinol-formaldehyde solution, gelling (polymerizing) the RF resin, supercritically extracting the water to prevent the porous structure from collapsing, and heating the polymerized-resin/carbon paper structure to convert the resin to a microporous carbon aerogel which is supported by the carbon paper. The paper also makes the structure strong, flexible and highly conductive. Since licensing the Livermore technology, CDT Systems has greatly reduced the cost of producing the electrode assembly (by roughly a factor of 30), primarily by replacing the supercritical extraction with a solvent extraction.

Unfortunately, even the improved electrodes are still too expensive. The high cost stems from three main factors: 1) the resorcinol used to make the high surface area electrode is expensive, 2) the surface area of the electrode are too low (which lowers the salt capacity of the electrode and increases the number of plates needed for a given duty), and 3) the solvent extraction step used to remove water from the gel is expensive (even if it isn't nearly as expensive as supercritical extraction).

TDA has recently invented a method of making porous carbon electrodes that addresses all of these problems: 1) The carbon is made from very inexpensive precursors, 2) the carbon has a combination of large pores that allow the ions easy access to the interior of the electrode and small high surface area pores to increase its working capacity, 3) the carbon is made without the need for an extraction step.

Our Phase II is designed to develop the formulations and processes needed to further improve the performance and reduce the cost of our electrodes (which is of course the reason that CDT Systems would adopt them), and provide the data needed to show their reliability, durability and manufacturability. Our proposed Phase II project has five main tasks: 1) Further decrease the cost of carbon the precursors by using less expensive sources of carbon and less expensive mesopore formers, 2) Support these materials on less expensive supports, 3) Test the physical and electrical performance of our electrodes and their durability, 4) Demonstrate that our production process can be carried out using production equipment on hand at CDT Systems, 5) Calculate the cost of producing our electrodes in CDT Systems' facilities.

2 Research Results

Electrode Performance. The electrodes were prepared by impregnating carbon paper with a solution of the carbon precursors followed by drying and carbonization in a box furnace. To test the performance of our electrodes, we built an apparatus that is identical to that used by CDT Systems to test their current RF based electrodes. The test apparatus consisted of a reservoir containing 10,000 ppm NaCl solution. Two electrodes are suspended in the solution. The electrodes are 2" x 3" and 1 mm thick, and 2" of the electrode is submerged in the NaCl solution. Contact to the dry end of the electrodes is made with alligator clips. The power system consists of a power source, relay and a resistor. The experiment is computer driven by Control EG software. The experimental sequence is to charge the electrodes at 1.2 V for 30 minutes and discharge the cell through a resistor and measure the voltage drop. Since the electrodes are all the same dimensions, we can directly compare the performance in term of energy (J/cc).

In Table 1, we compare the performance of electrodes made with different carbon precursors supported on the carbon paper substrate. The performance of TDA1 and TDA2 were similar to that of the current CDT Systems RF electrodes. One benefit of the TDA1 and TDA2 carbons is that the raw materials cost is less the half the cost of CDT's current RF based electrodes.

In contrast, the TDA3 and TDA4 carbon electrodes greatly exceed the performance of the CDT carbons. As shown in

Table 1. Extracted energy from carbon paper electrodes.

Sample	Energy (J/cc)
CDT	3.7
TDA1	3.7
TDA2	3.5
TDA3	5.9
TDA4	7.0

Table 2, the surface area as measured by nitrogen adsorption is approximately twice that for the CDT electrodes. Since the ion removal capacity also increased substantially, a large part of the increased surface area must have large enough pores to be accessible to the salt solution.

Since ion capacity per unit volume is the most important criteria for the electrodes, it is important to produce electrodes that have high density and high surface area. In addition the pores must be large enough for the solution to access the surface area. In Table 2 we show that the density of CDT's electrodes and TDA4 are similar but TDA4 has a larger surface area. By comparing the micropore volumes for the two electrodes, it is evident that TDA4 has much more microporosity than the CDT electrode. Since the micropores are smaller, this results in more pores per unit area and thus a higher surface area. The mesopore volumes are illustrated in Figure 3 showing that the CDT electrodes have much more pore volume in the mesopores range than the TDA4 carbon electrodes and the calculated BJH average pore diameter is also smaller for TDA4 compared to the CDT electrodes (Table 2). Even though TDA4 has less mesopore volume, most of the micropore volume must still be accessible to the salt solution since the ion capacity of TDA4 is much greater than the CDT carbon. As a result, although most of the pore volume is in the micropore range, we believe the mesopores create channel for liquids to enter the carbon and allowing access to the micropores resulting in greater utilization of the carbon.

Table 2. Properties of carbon paper electrodes.

Sample	Density	Pore Volume (cc/g)	Micropore Volume (cc/g)	BJH Average Pore Diameter (nm)	BET Surface Area (m ² /g)
TDA4	0.59	0.32	0.23	3.3	559
CDT	0.56	0.26	0.05	4.0	297

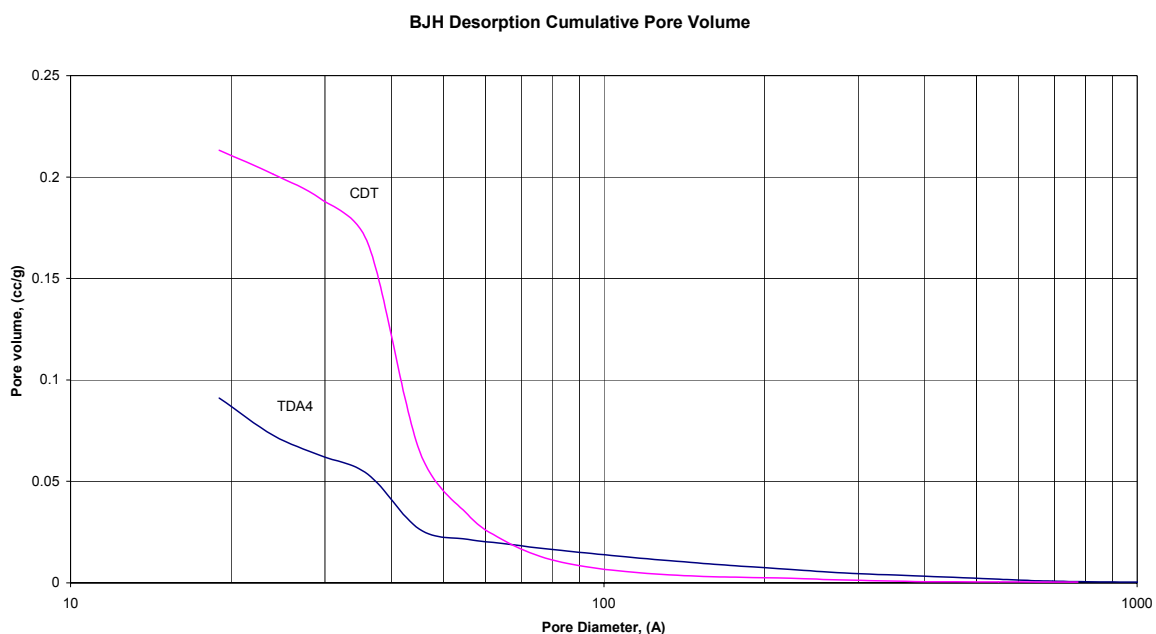


Figure 3. Pore volume versus pore size comparison for CDT and TDA4 electrodes. (17 angstroms is the lower limit of the instrument).

3 Conclusions

Thus far we have developed carbon electrodes that have almost double the ion capacity than that of CDT Systems' current RF electrodes and are made from materials that cost only 20% as much. Furthermore, the processing cost for making our electrodes is considerably less because we have eliminated the extraction step. Also, by eliminating formaldehyde for the formulation we have made the production process much safer, environmentally friendly, and easier to permit (formaldehyde is highly toxic and is a suspected human carcinogen). In addition, we believe that there is stillroom to further reduce the cost of the starting materials and increase the performance of the electrodes.

4 References

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