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CARBON-BASED ELECTRIC DOUBLE LAYER CAPACITORS FOR WATER DESALINATION

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ABSTRACT

In capacitive deionization (CDI), salt water is passed through two polarized electrodes, whereby the salt is adsorbed onto the electrode surface and removed from the water stream. This approach has received renewed interest for water desalination due to the development of new high-surface area carbon-based nanomaterials. However, there is currently limited understanding as to how electrode geometry, surface properties, and capacitance affect ion capture. In this work, we experimentally investigate various standard carbon-based electrode materials, including activated carbon and carbon cloths, as well as microfabricated silicon structures for CDI. Electrochemical characterization through cyclic voltammetry was used to determine the electrochemical properties of each material. In addition, a mini-channel test cell was fabricated to perform parametric studies on ion capture. By controlling electrode geometry and chemistry in these studies, the work helps elucidate transport mechanisms and provide insight into the design of optimal materials for capacitive deionization.

INTRODUCTION

Capacitive deionization (CDI) is a water purification technique achieved by the electrosorption of ions onto porous electrodes. Water passes through charged electrodes, causing the ions to electromigrate and adsorb on the electrode surface to shield the surface charge, as shown in Figure 1. This process subsequently reduces the concentration of the outlet stream. When the ions are in this charged state, energy is stored analogous to an electric double layer capacitor. By releasing the ions from the electric double layer into a purge stream, this energy can be reclaimed and the electrode surfaces can be cleaned for future adsorption cycles. Because this technique charges and discharges a series of electrochemical capacitors in a cycle, the theoretical efficiency should be very high,

especially for lower concentrations of feed solution such as brackish water.

To attain high capture efficiencies, however, the electrodes require both high conductivity and a high surface area. Research has typically focused on carbon-based electrode materials such as carbon aerogels, activated carbon, activated carbon cloth, and carbon nanotubes. Farmer demonstrated the feasibility of CDI using carbon aerogels with surface areas ranging from 400-1000 m²/g in the 1990s [1-3]. More recently studies have focused on modifications to activated carbon, activated carbon cloth, and carbon nanotubes for increased surface area for ion capture [4-7]. However, in all of these studies, there is limited understanding of the underlying electrode-electrolyte transport phenomena that can subsequently be used to tailor advanced materials for more efficient CDI.

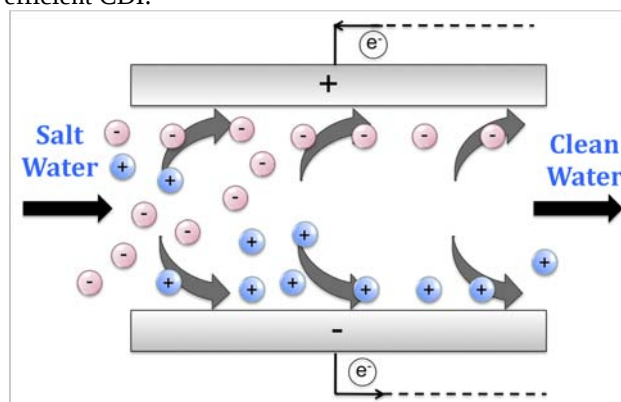


Figure 1. Schematic of capacitive deionization showing salt water flowing between two electrodes. By charging the electrodes, the ions adsorb onto the surface, thereby reducing the concentration of the output water stream.

Although macroscopically CDI appears to be relatively straight-forward, the ion transport locally within the electrode is not well understood. The modeling of CDI is challenging due to large applied surface potentials around 1 V (compared to the thermal voltage of 25.7 mV at 25°C), long charging times, complicated electrode geometry, and small, confined pore spaces where linear electrokinetic theory does not apply. Aside from a few studies [8-10], most of the research has been experimental and focuses on novel electrode synthesis, especially modifications to standard carbon-based materials. Most of these carbons, such as activated carbon and carbon cloth, contain tortuous and non-uniform pores that further complicate the ion transport.

Fortunately, the emerged interest of electrochemical capacitors for energy storage [11-13], has offered potential new opportunities and insights into CDI. Experiments suggest that ions may in certain cases desolvate to enter smaller pore sizes leading to a large increase in capacitance values [14]. Electrochemical characterization using cyclic voltammetry has shown large capacitance values. However, Li *et al.* demonstrated with ordered mesoporous carbons that even given a larger capacitance value, the ion capture was low due to the ordered pore structure [15]. A well-defined relationship between how the electrode pore structure and geometry affect the overall ability for a given material to adsorb salt has yet to be established.

The ability to understand ion transport within nanometers of the electrode-electrolyte interface can greatly enhance the ability to tailor materials to enhance transport into the pores. On the macroscopic level, this manifests itself as enhanced efficiency in electrosorption materials, which can help make CDI a more marketable desalination technology.

In this study, we initiated understanding ion capture with electrode materials for CDI. We investigated the electrochemical behavior of commercially available activated carbon and carbon cloth when applied as an aqueous capacitor. We also have examined the material's ability to absorb salt in a mini-channel flow experiment. We have subsequently examined the electrochemical properties of various controlled nano- and microfabricated silicon structures and tested them in a microchannel flow cell to further understand the ion adsorption process.

EXPERIMENTAL METHODS

In order to test the effectiveness of a given electrode material for desalination, both electrochemical cyclic voltammetry testing and conductivity measurements in a flow-through-capacitor channel were used. The materials tested ranged from commercially available carbon-based materials including activated carbon and carbon cloth, as well as fabricated silicon-based micro- and nanopillars.

Materials

Commercial carbon materials, including activated carbon cloth and activated carbon were acquired for testing. The carbon cloths from American Kynol ranged in specific surface

from 1000 m²/g to 2000 m²/g. Additionally, activated carbon samples from Maxwell Technologies, for commercially available supercapacitors were obtained with comparable surface area to the activated carbon cloths. SEM images of these materials are shown in Figure 2. In addition to the micron-sized features, these materials also exhibit a high density of non-uniform, tortuous pores ranging on average from 2 to 10 nm. These pores account for most of the increase in specific surface area.

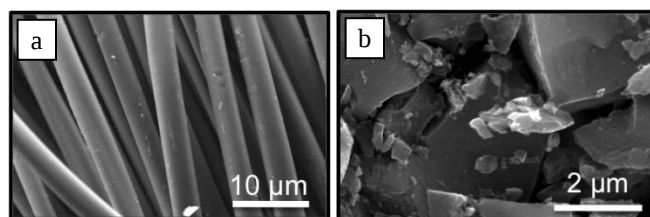


Figure 2 (a) SEM of activated carbon cloth, (b) SEM of activated carbon. In both (a) and (b), a network of tortuous pores exist on average of 2-10 nm.

In addition to the commercially available carbon materials, silicon based micropillars and nanopillars were fabricated. The micropillars are fabricated using standard photolithography and deep reactive ion etching. The resulting pillars are uniformly spaced 5 μm apart with 1.5 μm diameter and 5 μm height as shown in Figure 3. Using the specified geometry increases the planar surface area by a factor of 3. The nanopillars are fabricated using NIST standardized 50 nm polystyrene beads (Thermo Fischer Sciences) as a physical mask on highly doped silicon. The beads were suspended 1% by weight in an aqueous solution and mixed in a 1:1 solution with ethanol. The solution was spin-coated onto silicon wafers with a 330 nm thermal oxide layer. The wafers were subsequently etched using reactive ion etching. A gaseous mixture of SF₆ and O₂ etched through the oxide to create the nanopillars in the conductive silicon substrate. A cross-section of the nanopillars is seen in Figure 4b. The resulting nanopillars are on average 50 nm in diameter and 200 nm in height, distributed throughout the entire substrate. Although the spacing is not controlled like the templated micropillars, the increase in surface area can be approximated to be about 13 times the planar area at maximum.

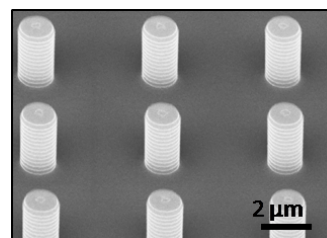


Figure 3. SEM image of the silicon micropillars. The pillars are spaced 5 μm apart with 1.5 μm diameter and 5 μm height.

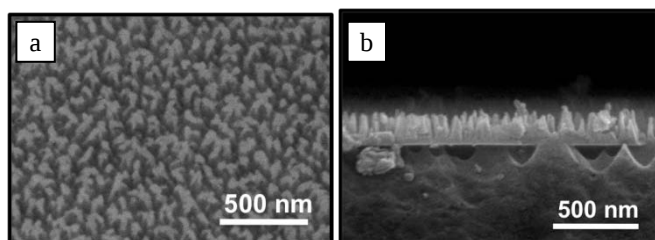


Figure 4. SEM images of the silicon nanopillars showing (a) top view and (b) cross-section. The pillars measure about 50 nm in diameter and 200 nm in height.

Electrochemical Characterization

Cyclic voltammetry testing using a potentiostat (model 1470E, Solartron Analytical) was used to characterize the electrical capacitance of each material. The measurement sweeps through a series of voltages as current is monitored. The capacitance, C , is then measured by the standard relation:

$$C = \frac{I}{dV/dt}$$

and is averaged over the entire scan where I is the current and dV/dt is the voltage scan rate. A 1 M NaCl electrolyte was used with Celgard 5401 aqueous-specific polypropylene separators. The scans were performed at sweep rates of both 10 mV/s and 50 mV/s.

Flow Cell Design

A mini-flow channel was first constructed to study the effect of capacitor charging on changes in bulk salt concentration. The various carbon materials were made into 3 cm by 3 cm square electrodes and integrated into the 10 cm by 3 cm by 3 mm high channel. A test solution of 1 mM NaCl filled the channel and a potential was applied across the electrodes ranging from 1-6 V (It should be noted that when applying voltages larger than the standard breakdown of water at 1.2 V, no electrolysis was observed. However, this does not eliminate possible bubble formation within the electrode, which is obscured from view.). After the electrodes were charged (~15 minutes), the solution in the channel was purged while measuring the bulk solution conductivity using a standard conductivity probe (CON-BTA Conductivity Probe, Vernier). A mini-flow channel schematic is shown in Figure 5.

A current redesign of this channel, scales down this process and integrates localized conductivity sensors into a microchannel setup. The microchannel is fabricated in silicon with a 200 nm platinum layer, applied by electron beam deposition, in specified regions for conductivity sensing. In future studies the absorption electrodes will also be deposited or fabricated on the silicon surface. As the salt water flows through the channel, the absorption electrodes can be actively charge as the conductivity sensors detect any concentration changes. Compared to the original channel size, the scaled-down microchannel is 6 cm by 2 cm with a 200-300 μm gap. The smaller channel dimensions enable more sensitive

measurements and can therefore detect smaller changes in the solution bulk concentration.

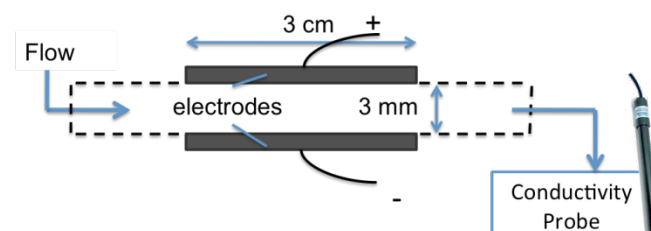


Figure 5. Illustrative schematic of the mini-flow channel set up. Salt water flows through the channel and after charging of the electrodes, the concentration of the solution is measured by a conductivity probe.

RESULTS AND DISCUSSION

Figure 6a shows cyclic voltammograms for the different materials. The largest capacitance of the carbon materials tested was the 2000 m^2/g activated carbon cloth with a specific capacitance of 40 F/g, followed by the 1000 m^2/g activated carbon cloth with 32 F/g, and finally the activated carbon with 25 F/g. The activated carbon electrodes, however were very hydrophobic due to the presence of a hydrophobic PTFE binder. In comparison, the activated carbon cloths easily wicked in the salt solution. Although the surface areas are comparable as well as the underlying microstructure, we speculate that the underperformance of the activated carbon is likely attributed to the hydrophobic binder.

Similarly, when these materials were tested in the mini-flow cell, the highest capacitance activated carbon cloth exhibited the largest amount of salt absorption, while the hydrophobic activated carbon had the lowest amount of salt removal for a given applied voltage. Although these three materials obey a linear trend between the capacitance and salt absorption as seen in Figure 6b, the salt absorbed is approximately three orders of magnitude lower than what is expected with the equivalent surface charge. This discrepancy can be in part attributed to the resistances of the electrodes and electrode-electrolyte interface. However, the long electrode charging times (compared to standard capacitor characteristic charging times) may indicate that there are additional ion transport limitations due to the tortuous porous network in the activated carbons-based materials which reduces the materials' effectiveness for ion capture.

Electrochemical testing was also performed on the silicon-based electrodes shown in Figure 6c. The average capacitance values were determined using a 1 M NaCl solution and a sweep rate of 50 mV/s. In each case, the electrodes were cycled 30 times, with the average capacitance values consistent across a 10 mV/s and 50 mV/s scan rate. The specific capacitance for the unpatterned silicon was 1.6 mF/g, the micropillars was 5.2 mF/g, and the nanopillars was 26 mF/g. The micropillars had a threefold increase in surface area to the unpatterned silicon, which is approximately matched by an equivalent increase in capacitance. The nanopillars, however, exhibited an increase in capacitance larger than the increase in surface area. Whereas

the surface area increased by a factor of 13, the capacitance value is over 16 times that of the unpatterned silicon.

We speculate that this anomalous increase in capacitance may be attributed to a variety of factors. First, the estimates in surface area are difficult due to the non-uniform surface distribution of the nanopillars. In addition, there may be residual sulfur on the electrode surface after fabrication due to exposure to SF_6 plasma. Sulfur left on the surface may react in water at standard potentials of 0.447 V. The peak on the cyclic voltammogram at around 0.5-0.6 V may be an indication of this Faradaic reaction, thereby increasing the capacitance through pseudocapacitance. Lastly, there may also be geometrical advantages at this length scale, which can aid in the ion transport through restructuring of the electric double layer. However, further work will be performed to elucidate this large change in capacitance.

Further tests are currently being conducted to establish the magnitude of salt capture on the controlled silicon structures in the microchannel setup, in order to investigate the correlation with the measured capacitance. Given a surface structure that is more ordered than that of the carbon-based materials, we speculate that the ion capture from these basic geometric structures should be approximately on the same order of magnitude with the surface charge excluding any effects from Faradaic reactions.

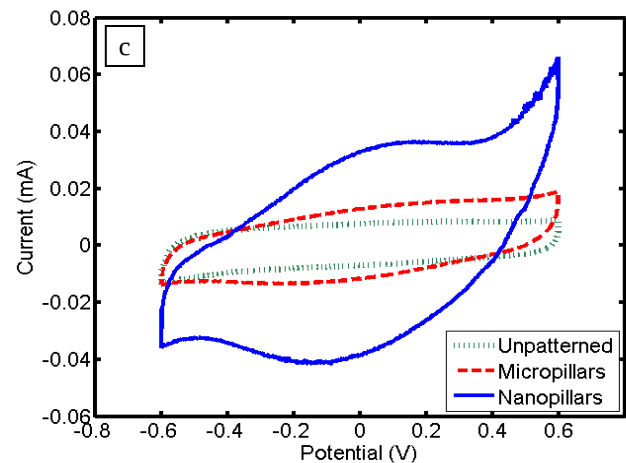
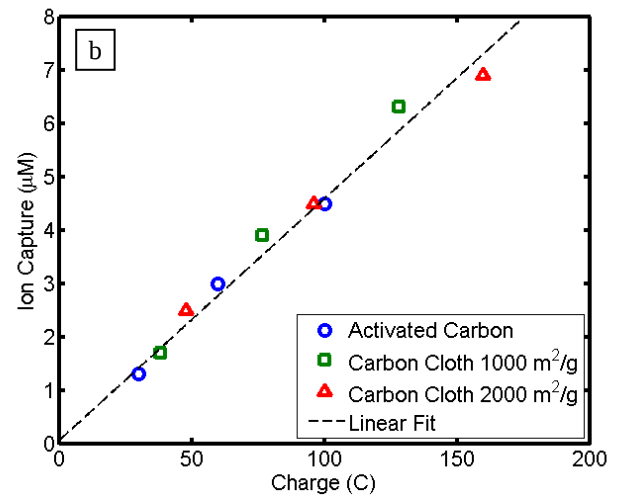
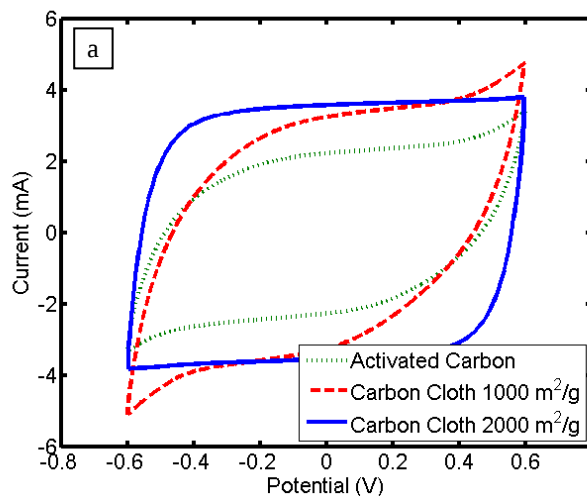


Figure 6. Experimental results. (a) Cyclic voltammograms of the carbon cloths and activated carbon materials. In each test, an electrolyte of 1 M NaCl was used with a sweep rate of 10 mV/s. (b) Ion capture with a 1 mM input NaCl solution for the carbon-based electrodes in the mini-flow channel experiment after scaling by the capacitance. The linear fit indicates that regardless of the type of carbon material, the relationship between applied surface charge and ion capture is equivalent. (c) Cyclic voltammograms of the silicon-based materials. Each test used a 1 M NaCl electrolyte with a sweep rate of 50 mV/s.

CONCLUSION

Commercially available activated carbon and carbon cloth were investigated for effectiveness as electrode materials in CDI. Electrochemical characterizations were performed to determine capacitance values. These materials were also integrated into a mini flow channel experiment to determine the decrease of bulk solution salt concentration through surface ion adsorption. We determined that the amount of ion adsorption is three orders of magnitude less than the equivalent electrode surface charge. We speculate that this decrease in expected salt capture is due to ion transport limitations created by geometrical constraints within the material microstructure.

To further investigate the relationship between geometry, capacitance, and ion capture, we fabricated micro and nano structures on highly conductive silicon substrates and performed electrochemical characterization of these materials. Further studies will focus on integrating these materials into a microchannel setup for controlled measurements of ion capture and relating the ion capture to transport limitations.

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