Characterization and Performance of Vertically-Aligned Carbon Nanotubes in Capacitive Deionization Systems

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Dedicated to my parents.
For all the math lessons at the kitchen table.
For letting me go as far as I could.
For your unbounded love and support.
This milestone is for you.

And for Mike.
Couldn’t have done it without you.
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Abstract

Less than 1% of the world’s 1.4 billion km$^3$ of water is available freshwater. In contrast, 98% of the world’s water is in the form of brackish and seawater (1000-35,000 ppm or 10-600 mM NaCl concentration). Desalination can increase our water supplies, generating sufficient water for household, industrial, and agricultural uses and mitigating the escalating water crisis. As one strategy for water desalination, capacitive deionization (CDI) could prove optimal for brackish water treatment, due to its higher energy efficiencies compared to reverse osmosis and its more inherent resistance to fouling. CDI is a developing technology where adsorption capacity and salt removal rates into porous, tortuous carbon electrodes is still low. Previously, a breadth of carbon material electrodes have been investigated for CDI, due to their high surface area to volume ratio, high conductivity and non-corrosive property in salt water. However, many carbon materials have tortuous pores making it challenging to decouple the role of pore diameter on salt adsorption rate. To simplify the characterization of the electrode, we took advantage of vertically-aligned carbon nanotubes (VA-CNTs). VA-CNTs are an exciting material for investigating the coupling of the electrode and ion transport in a flow-cell due to the ability to manipulate the inter-CNT spacing, to study changes in the ion transport rate as a function of geometry, while maintaining minimal tortuosity and intrinsic capacitance. In this work, we utilized monolithic VA-CNT forests to investigate the coupling of device geometry and porous electrode design on the performance of flow-by CDI devices, specifically examining changes in salt adsorption rate, salt adsorption capacity, and salt rejection.

First, we designed and characterized VA-CNT electrodes using standard three-electrode beaker experiments. These VA-CNTs were grown using a standard chemical vapor deposition of ethylene on silicon wafers with iron catalyst. In addition, we mechanically densified these forests to achieve densities greater than 25x the density of as-grown forests. We measured the capacitance and impedance spectra of VA-CNT electrodes in 1M NaCl, finding that they have a capacitance of 22-35 F/g or 7-11 μF/cm$^2$. From the impedance spectra, we used a modified transmission line model to calculate the inter-CNT spacings which are up to 100 nm in sparse forests,
and as low as 25 nm in our high volume fraction forests. This simple electrochemical approach can be used to characterize electrodes and predict performance in flow-by CDI devices.

Second, we used a flow-by CDI experimental set up to study the role of varying voltages, electrode thicknesses, and CNT densities, on desalination performance. We found that in a 1 mM NaCl solution, CNT electrodes adsorbed from 4-8 mg salt/g carbon, at rates of 0.2-0.4 mg/g-min. Through densification or reduction in electrode thickness, we could maintain our gravimetric salt adsorption while increasing or reducing the salt adsorption rate proportionally to the diffusion time constant. This demonstrated that desalination in these cells is limited by diffusion from the flow channel into the electrode. These investigations provide a framework for studying the performance of a CDI cell for a given electrode.

Finally, we combined the experimental investigations with an advection-diffusion model to inform the design of carbon electrode materials for optimal ion adsorption and throughput in a flow-by CDI device. We developed a model that is dependent on device specification parameters (system volume, flow rate, inlet and outlet water quality) and independent of electrode material, to generalize the design of a cell for any given requirement. We showed that decreasing the advection-diffusion Péclet number and increasing the aspect ratio of the electrode compared to the channel space yields the highest salt rejection. In addition, tuning the duty cycle for salt rejection instead of complete electrode charging can yield faster water production rates and optimal salt rejection.

This thesis provides a framework for the selection and design of flow-by CDI devices for optimal salt rejection for given specifications. This investigation uses VA-CNTs as a proof-of-concept approach which can be extended to the multitude of porous carbon materials used in existing devices.

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Chapter 1

Introduction

Less than 1% of the world’s 1.4 billion km$^3$ of water is available freshwater [1]. 98% of the world’s water is in the form of brackish and seawater (1000-35,000 ppm or 10-600 mM NaCl concentration). Desalination can increase our water supplies, generating sufficient water for household, industrial, and agricultural uses and mitigate the escalating water crisis. In order to keep costs low and sustainable, however, minimizing the energy expenditure is essential. The minimum energy required to desalinate arises from reversing the Gibbs free energy of mixing salt and water, which is approximately 0.8 kWh/m$^3$ for seawater (600 mM at 298K) and 0.07 kWh/m$^3$ for brackish water (50 mM at 298K). Therefore, desalination of brackish water is less energy intensive compared to seawater. The United States consumes 111.7 km$^3$/yr in groundwater, over 25% of its net water usage [2]. Saline groundwater is estimated to comprise 12.9 million km$^3$ or 1% of Earth’s water resources [3]. Across the United States, brackish groundwater exists abundantly at shallow depths, <305 meters from the surface [3]. Through energy-efficient desalination of groundwater, we can significantly increase resources nationally, and possibly double the globe’s accessible resource.

1.1 Desalination Overview

The three most common approaches to desalination are phase change, reverse osmosis, and electrodialysis [1]. Of phase-change approaches, multi-stage flash (MSF), where
water is boiled and the condensate is collected, is the most prominent, comprising 44% of the world’s desalination capacity [1]. However, MSF is very energy-intensive because water is converted from liquid to vapor and requires a large latent heat. Current MSF systems consume 23.9-96 kWh/m$^3$ [1], which is significantly larger than the minimum Gibbs free energy required for desalination. At present, reverse osmosis (RO) systems, where fluid is pressurized to flow across semi-permeable membranes which reject salt, have been the front-runner for desalination plants. RO is the most energy efficient of industrial technologies, consuming as little as 3.6 kWh/m$^3$ generated freshwater [3]. However, RO membranes are sensitive to the water conditions. They are prone to fouling in the presence of heavy metals, inorganic salts, and sulfides [4], which is prevalent in groundwater from industrial processes and minerals in the rock-bed. In order to minimize fouling, anti-scaling, anti-foaming, and anti-corrosive chemicals are added to the brine. Membrane cleaners, such as disinfectants, have been shown to be toxic to cell membranes, hurting fish, invertebrates, and other sea life [3]. RO systems need water pre-treatment and additives to operate over long periods of time. Finally, electrodialysis (ED), in which saline water flows between ion-exchange membranes in a perpendicular electric field, creating saline and potable streams, comprises ~5% of the world’s desalination capability [1]. ED is a charge-based approach to desalination where ions flow between channels separated by ion-exchange membranes, and are sorted in response to an applied electric field [5]. However, ED is not as economically competitive as RO, and membranes can be expensive with short lifetimes [5].

While MSF and RO are effective desalination systems they often require large footprints and infrastructure for operation. ED is more promising for smaller-scale systems though more work may be needed to reduce membrane costs and increase lifetime. There is an opportunity for developing small-scale desalination systems, especially for brackish groundwater treatment, that do not require membranes or high energy/infrastructure. Capacitive deionization may be an additional approach to removing salt in water treatment.

Capacitive deionization (CDI) is a charge based system for desalination (Figure 26...
A voltage is applied across high-surface area electrodes, driving charged ions in solution (such as sodium and chloride, but also heavy metals and other charged molecules) to adsorb in the electric double layer at the electrode surface. The desalinated bulk water is collected, and the cell is then discharged. In brackish water (<100 mM NaCl), CDI can be more efficient compared to RO systems. CDI has 75-90% efficiencies at low concentrations, because the desalination component only requires adsorption/desorption and is highly reversible [7]. In contrast, state-of-the-art RO membranes are only ∼40% efficient [8]. Preliminary bench-top CDI experiments have shown energy consumptions of 0.5 kWh/m$^3$ for 30 mM NaCl solutions, half that of typical RO systems in brackish water [9]. In addition, CDI can be used to remove pollutants beyond sodium chloride. Xu et al. has shown CDI to remove over 98% of iron, chromium, uranium, copper, nickel, zinc, and lead from wastewater with no scaling observed [10]. In addition, electrochemical techniques can be used to kill bacteria [11] or simply remove them through adsorption [12], to reduce/oxidize organic compounds polluting groundwater [13]. Therefore, CDI is well-positioned for treatment of brackish groundwater. It is competitive with existing technologies in terms of energy consumption, and is intrinsically more resistant to scaling than membrane filtration. This suggests that CDI can be reliable long term for brackish water desalination.

In this chapter, we will introduce CDI, outline promising work that has been accomplished to date by scientists and engineers, and finally suggest opportunities for new understanding and development.
1.2 Capacitive Deionization for Water Desalination

Early development of CDI focused on demonstrating a proof-of-concept and understanding the mechanism behind desalination. In the 1960s and 70s, the deionization of water through an applied electric field using graphitic current conductors was demonstrated [14, 15, 16]. Early researchers believed that deionization occurs through Faradaic reactions on the electrode surface [17], creating acidic and basic groups which could react with NaCl [18]. This was later replaced with double layer theory [16]. A detailed approach to model development will be provided in Chapter 4. Here, we provide a brief conceptual understanding of double-layer charging, in order to better understand the opportunities in CDI research.

1.2.1 Electric Double Layer Theory

In CDI, salt removal from the bulk occurs through the storage of ions at the electrode surface in the electric double layer (EDL). The physics of the EDL can provide insight into the relevant material parameters for desalination. In this section, we outline the basic Gouy-Chapman-Stern theory [19], in order to provide insight into how much salt can be removed during a CDI cycle and implications of the theory on electrode design. Some of this discussion is adapted from my master’s thesis [6].

When a potential is applied at an electrode surface, \( \phi_0 \), charge builds up at the surface. At the electrode-solution interface, at \( x = 0 \), counterions from the solutions build up at the surface to balance the excess electrical charge of the electrode. Moving away from the surface, as \( x \to \infty \), this ion concentration decreases, returning to bulk concentration, \( c_\infty \). This is the formation of the double layer, depicted in Figure 1-2.

A simple analysis of the salt distribution in the double layer can be determined by starting with the Nernst equation and Boltzmann distribution, where \( c \) is the concentration, \( \phi \) is the potential, \( kT/e \) is the thermal voltage, and \( z \) is ion charge.

\[
\ln \left( \frac{c(x_2)}{c(x_1)} \right) = -\frac{ze [(\phi(x_2) - \phi(x_1))]}{kT} \tag{1.1}
\]
Figure 1-2: Schematic of the Gouy-Chapman-Stern double layer and a representative distribution of ions in the diffuse layer for $\Delta \phi_D = 10$ mV and bulk concentration $10\text{ mM}$.

\[
c(x_2) = c(x_1) \exp \left\{ -\frac{z e [\phi(x_2) - \phi(x_1)]}{kT} \right\}
\]

(1.2)

In order to relate charge and potential we use Poisson’s equation. Derived from Gauss’ law, Poisson’s equation gives:

\[
\frac{d^2 \phi}{dx^2} = -\frac{\rho_e}{\varepsilon}
\]

(1.3)

where charge density $\rho_e = \sum c_i z_i F$ and $\varepsilon$ is the permittivity. The boundary conditions for this system are:

\[
\phi(x \to \infty) = 0
\]

(1.4)

\[
\phi(x = \lambda_s) = \phi_0 - \Delta \phi_S
\]

(1.5)

where $\lambda_s$ and $\phi_S$ are the Stern layer thickness and potential drop, respectively. Summing from the surface of the electrode to the bulk of the solution ($x = \lambda_s$ to $x \to \infty$), and combining equations [1.3] and [1.2] we arrive at the Poisson-Boltzmann equation. For an ion solution where the valency is 1:1, such as sodium chloride, the Poisson-Boltzmann equation is:

\[
\frac{d^2 \phi}{dx^2} = \frac{F c_\infty z}{\varepsilon} \sinh \left( \frac{z e \phi}{kT} \right)
\]

(1.6)

The above analysis was conducted independently derived by Gouy and Chapman, and comprises the Gouy-Chapman (GC) theory. To calculate the surface charge density,
we integrate equation 1.6

\[ q = \int_{0}^{\infty} \rho \, dx = -\varepsilon \int_{0}^{\infty} \frac{d^2 \phi}{dx^2} \, dx \]  

(1.7)

As the theory shows, the adsorption of ions in the electric double layer is dependent on the surface charge. In addition, electrode potential and solution conductivity are important to charging kinetics in CDI, as experimentally investigated early on by Oren et al. [20, 21, 22, 23]. Synthesizing high surface area materials, with high electrical conductivity, is essential for a CDI electrode. The higher the gravimetric/volumetric surface area, the larger the concentration of salt can be removed from the bulk. In fact, early research was initially suspended due to the lack of high surface area materials available, though Johnson et al. suggested materials with volumetric surface area of 230 m²/cm³ would be sufficient [16]. As high surface area materials were invented in the 1980s and 1990s, CDI research was renewed. The monolithic carbon aerogel, with surface areas between 400-1100 m²/g [24], began to be utilized in large stack prototypes [24, 25, 26, 27, 28, 29]. Since then, a wide array of materials have been developed and studied in CDI. However, as Porada et al. puts it, the question still remains, "What is the best material for CDI?" [9].

1.2.2 Carbon-Based Electrode Materials for CDI

Materials for CDI need large capacitance, which comes from having high electrical conductivity for easy surface polarization and high surface areas. In addition, materials that have fast diffusivity can yield favorable desalination rates. In order to have high-performance desalination, finding a suitable electrode material is key.

Previously, many carbon materials have been studied for CDI: activated carbon [30, 31, 32, 33], carbon cloth [34, 35], ordered mesoporous carbons [36, 37], carbon aerogel [27, 38, 39, 40, 41, 42] and xerogel [43, 44], carbide-derived carbons [45], carbon nanotube and nanofibers [46, 47, 48, 49, 50, 51, 52, 53, 54], graphene [55, 56, 57, 58, 59, 60, 61], among many others [62], some depicted in Figure 1-3. These materials have surface areas ranging from hundreds to thousands of m²/g. However,
Figure 1-3: Various carbon materials used in CDI research. a) carbon nanotube and nanofiber composite, b) activated carbon cloth, c) carbon aerogel, d) ordered mesoporous carbon. Figure originally in [1].

Salt adsorption capacity has also been very variable between these materials. While surface area is important, it is not the only factor in generating high salt adsorption. Recently, Porada et al. showed that the presence of micropores were important for increasing salt adsorption [45]. Thus, materials development has moved towards hierarchical carbon materials, making use of macropores and micropores for high salt adsorption materials [62]. The greatest reported salt adsorption capacity to date has been in a CNT-graphene composite with adsorption up to 26.4 mg/g [63]. Figure 1-4 shows general trends in CDI electrode salt adsorption capacity. We observe that the move to composite materials has yielded much larger capacitances than single materials.

While these gains are promising, these materials are highly complex. They are tortuous, have varying porosities with micropores that are too small for classical double layer theory to be applied, and have adsorption surface areas that are difficult to characterize (BET analysis from gas adsorption yields surface areas that are not necessarily equivalent to the area available for ion adsorption in electrolyte). In order to understand the coupling of the electrode material and device design, we propose using a very simple material to minimize assumptions about desalination and gain a more holistic view of CDI device design.
1.3 Scope of Thesis

The goal of this thesis is to design a framework to better understand how to design a CDI device for maximum desalination performance. This work builds on groundwork laid during my master’s thesis. In order to do this, we propose using vertically-aligned carbon nanotubes (VA-CNTs), a simple carbon structure, as an electrode material. We can use VA-CNTs to easily manipulate thickness and density to manipulate electrode properties. By methodically changing CDI system design, we can better understand how CDI device sizing coupled with the electrode will ultimately define the desalination output of a given device.

In the second chapter, we will study electrode charge and capacitance of VA-CNTs. In addition, we develop a novel approach to characterizing the inter-CNT spacing of VA-CNT forests of varying densities in situ. We can use these properties to better characterize the diffusivity and tortuosity of electrodes, as well as the surface area to volume ratio of the material.

In the third chapter, we demonstrate, for the first time, the use of VA-CNT electrodes in CDI devices. By varying material properties we demonstrate our ability to control desalination rates and effective adsorption. In addition, we examine shortcomings of VA-CNTs with respect to existing materials.

In the fourth chapter, we propose a desalination criteria for performance and
develop a holistic advection-diffusion model that captures CDI device kinetics without the computationally-intensive double-layer equations. We demonstrate both in theory and experiment, that tuning CDI flow parameters and the electrode-thickness to gap-thickness ratio can drive CDI systems to high performance. This model is agnostic to electrode material; thus, it can be used for nearly any type of CDI material.

Finally, we will summarize the main contributions of the thesis and possible extensions and directions for new research.
Chapter 2

Electrochemical Characterization and Porosimetry of VA-CNTs

2.1 Motivation

Electrochemical systems such as capacitors and batteries utilize vertically-aligned carbon nanotubes (VA-CNTs) to achieve high energy and power densities \cite{65}. Analogously, in water treatment systems, high ion electrosorption capacities and rates of removal are desired \cite{64, 66}, which may be possible with VA-CNTs. Accordingly, these materials have a large effective surface area typically 400 m$^2$/g \cite{67} in contact between the electrode and electrolyte leading to a high density of ion adsorption sites for large double layer capacitance \cite{68}, as in supercapacitors and CDI devices, or large number of sites for redox reactions as in pseudocapacitors and batteries. In addition, VA-CNT forests have minimally tortuous geometries, which can lead to significant power densities due to the presence of many easily accessible electrolyte pathways from the bulk solution to the surface of the electrodes \cite{67}. This can lead to high ionic conductivity and thereby allowing for fast transport of ions \cite{65}. A previous study comparing VA and unaligned CNT electrodes of similar thickness demonstrated that ordered, vertical orientation could have over 20 times faster charging \cite{69}. VA-CNT electrodes have also demonstrated competitive supercapacitances of 50-200 F/g or 50-130 F/cm$^3$ to double layer capacitance from 6-50 $\mu$F/cm$^2$ \cite{70, 71, 72, 73, 69}.
However, 1D arrays tend to be sparse, and increasing packing density to improve device performance has been of interest in many applications [74, 75, 76]. Densification of VA-CNT forests in supercapacitors [77] has led to volumetric capacitance gains directly proportional to the degree of densification, and that gravimetric capacitance is invariant with densification [78, 73]. Correspondingly, VA-CNT electrodes seem promising for capacitive deionization applications. However, current carbon electrodes may be under-utilizing the total available surface area due to the use of binder during synthesis or the tortuosity of the material causing transport limitations [9]. Elsewhere, VA-CNT forests have been investigated as a platform for pseudocapactive coatings [68, 78] and Li-ion batteries [79, 80, 81, 82], achieving capacities as high as 3300 mAh/g [82] (where the theoretical limit is 4200 mAh/g). Many of these studies have made use of 1 mm thick VA-CNT electrodes for high adsorption capacity, but have lower power densities than their thinner counterparts [73, 82]. This leads to an optimization question of how to design electrochemical devices with low overall weight and volume with high energy and power densities.

The rate capability of an electrode is dependent on the ionic conductivity of the pore, which is proportional to the cross-sectional area of the pore and inversely proportional to thickness [83]. Therefore, in order to design a high-performing electrochemical device, typically electrodes are thin (hundreds of microns) and have small pores (sub-2 nm to tens of nm) [84]. This can lead to a device requiring more cells to achieve the same ion adsorption or energy, and subsequently a more massive or larger overall device due to additional current collectors, spacers, etc [82]. VA-CNT electrodes provide the ability to easily vary the electrode thickness (height of carpet is proportional to growth time), and packing density leading to a reduction in the inter-CNT spacing, $\Gamma$. This control will enable us to study changes in the ion transport rate as a function of geometry, while maintaining minimal tortuosity and intrinsic capacitance. By characterizing $\Gamma$ of an electrode we can predict electrode performance for a variety of device and find optimal geometries for complete devices. However, in order to explore the role of $\Gamma$, we first need to consider how best to determine and quantify the packing morphology.
In sparse 1D nanostructure arrays, typically scanning electron microscopy is used to characterize the diameter of pores and interspacing [74, 85, 86, 87]. In VA-CNT forests where the features are finer, many techniques are used to characterize the alignment of forests and the diameter of nanotubes [88], but few quantify the interspacing. Typically, the surface area, diameter, and volume of pores in VA-CNT forests are calculated using Brunauer-Emmett-Teller (BET) theory (e.g., gas adsorption isotherm analysis). A limitation however is that gas adsorption measurements tend to include both the inner and outer surfaces of the nanotube [89], though typically only the outer surface area is accessible to the electrolyte [67]. In addition the quantitative pore size distribution from BET analysis is typically accurate from 1.5-15 nm [90], which is a smaller range than predicted CNT interspacings. In VA-CNT membranes, it is possible to measure the pore size distribution using varying diameter solute rejection [91], but this approach is vulnerable to leaks in the membrane. Another approach for estimating interspacing has been based on calculating the mass density, and average CNT characteristics such as height, inner diameter, and outer diameter in a sample (measured through transmission and scanning electron microscopy (TEM and SEM, respectively) characterization) [73, 89]. These values have been used either by assuming an ideal packing geometry [73, 77], or more recently with a continuous coordination number model [92], to predict an approximate $\Gamma$. While these theories can provide an approximate value of interspacing, they assume each nanotube is perfectly straight and therefore do not predict a large dispersion in inter-CNT spacing in a forest. However, recent stochastic modeling of VA-CNT forest growth has suggested that waviness of the nanotubes, leads to large dispersion [93], and is reduced as a function of increasing packing proximity [94]. More recently, SEM imaging of a cross-section has been used with image analysis to define the front-most plane based on the brightness of a CNT, to measure spacings along cross-sections of carpets [92]. However, these methods are limited to small regions of the sample (micrometer range) [95], and may not capture the macroscopic properties of the forest. In addition these methods are time-consuming and highly destructive, which prevent samples whose morphologies were characterized from being used in subsequent experiments.
In this chapter, we show that electrochemical impedance spectroscopy (EIS) can offer *in situ* non-destructive characterizations to determine the morphology of 1D nanostructure arrays and $\Gamma$ over the entire measured sample. In this study we use VA-CNT forests which provide the ability to easily vary the packing density through mechanical densification [77] leading to a reduction in the average inter-CNT spacing, $\Gamma$. Using a simple three-electrode beaker system, we conducted electrochemical experiments on VA-CNT carpets. We determined the double layer capacitance $C_{dl}$ of the CNT surface using cyclic voltammetry to obtain a capacitive operating voltage window and potentiostatic experiments to measure charge. We then used EIS to study the frequency response of the electrodes. By combining these measurements with a mathematical model for porous electrodes, we were able to obtain the average interspacing $\Gamma$, and the dispersion of the interspacing (i.e., standard deviation), $\sigma$, of VA-CNT carpets of varying densities. This approach can be extended to other 1D nanostructure arrays in order to quantify the average and dispersion of interspacings and predict specific device performance.

### 2.2 Methods

We synthesized and densified VA-CNT forests to study samples of varying porosity. The sample capacitance and frequency response were measured using cyclic voltammetry, potentiostatic testing, and impedance spectroscopy in order to analyze the inter-CNT spacing.

#### 2.2.1 VA-CNT Synthesis and Characterization

We synthesized $1 \times 1 \times 0.1$ cm VA-CNT carpets using chemical vapor deposition (CVD), using the procedure described by Stein *et al.* [95]. The carpets were grown on top of an iron catalyst in an ethylene and water vapor environment, yielding 1 mm tall carpets [95]. Water vapor flows through the CVD chamber following growth causing the forest to delaminate, separating the CNTs from the growth substrate. The CNTs were previously characterized as multi-walled (average of 5 walls), having
Figure 2-1: VA-CNT porosimetry study utilizing impedance spectroscopy \((Z(\omega))\) to assess morphology. a) SEM images of VA-CNT forests of varying volume fractions i) 1\%, ii) 2\%, iii) 5\%, iv) 10\%. Scale bar is 0.5 \(\mu\)m. b) (left) A three electrode beaker experiment is used to study the inter-CNT spacing, \(\Gamma\), in a forest. (middle) The impedance \(Z\) response is a function of the voltage input frequency \(\omega\) and \(\Gamma\). (right) The morphology is modeled from theoretical coordinations \(N\) where \(\Gamma\) of the pore is an average of the minimum and maximum inter-CNT spacing in a given unit cell. Figure published in [96].

an average inner diameter, \(d_i \sim 5\) nm [97], an outer diameter, \(d_o \sim 8\) nm [97], an average volumetric density, \(\rho \sim 1.7\) g/cm\(^3\) [95], and an average specific surface area of \(\sim 780\) m\(^2\)/g [89]. We measured the heights of the carpet, \(l_p\), using SEM (Merlin, Zeiss) and optical microscopy (Axiotech, Zeiss). We measured the mass, \(m\), using a microbalance (Discovery, Ohaus) in order to calculate the total number of CNTs in a sample, \(n_{cnt} = 4m/\rho l_p \pi d_o^2\). The available adsorption surface area was calculated from the total outer wall surface area of the CNTs as \(ASA = \pi d_o l_p n_{cnt}\). The volume fraction \(V_f\) of a forest is defined as the ratio of CNT volume to the total volume. Typically, the initial forest has a \(V_f\) of \(\sim 1\%\) [97]. Through mechanical densification [77], we increased the density of grown forests from \(1 - 3 \times 10^{10}\) tubes/cm\(^2\) to \(4.5 \times 10^{11}\) tubes/cm\(^2\), i.e., up to \(V_f \sim 25\%\). figure 2-1(a) shows with increasing \(V_f\), both \(\Gamma\) in the forest and \(w\) of the CNTs is reduced, similar to samples used in previous work [77, 95, 97]. With these samples, we can study the change in \(\Gamma\) and \(\sigma\) with a large range of densities.

2.2.2 Three-Electrode Electrochemical Testing

We conducted electrochemical experiments using a three electrode set up with a VA-CNT forest working electrode, Ag/AgCl reference electrode (Beckman Coulter, 3.5
Figure 2-2: Experimental set up. a) Schematic of working electrode holder: the VA-CNT forest is mounted to a Pt foil current collector using acrylic plates and a plastic mesh to constrain the forest against the current collector. b) Image of working electrode set up (front view), scale bar = 1 cm, and c) three-electrode cell set up with working electrode, Pt counter electrode, and Ag/AgCl reference electrode, scale bar= 1 cm.

VA-CNTs synthesized in a CVD process are typically hydrophobic. In order to wet the electrodes, we first dipped samples in isopropanol alcohol (IPA) and then subsequently into IPA diluted in deionized water solutions of varying ratios (e.g., 75% IPA, 50% IPA, 25% IPA, 0% IPA) until IPA was removed from the solution. Then, we immersed the samples in 1 M NaCl experiment solution for one hour before testing to ensure the electrodes were saturated with electrolyte prior to testing. We conducted experiments in 1M NaCl to ensure there was no significant concentration change in the bulk solution during electrochemical experimentation.

We used cyclic voltammetry (CV) at a ramp rate of 10 mV/s to determine the
Figure 2-3: Electrochemical characterizations. a) Cyclic voltammograms (1 M NaCl and 10 mV/s) indicating a capacitance window from 0 to 0.5 V vs Ag/AgCl. b) DC charge vs potential shows that sample capacitance varies between 7-12 $\mu$F/cm². c) Nyquist plot of EIS data and model at 0 ± 5 mV. Data in colored symbols compared to the porosimetry model fit (equation (2.2)) given by open symbols and black lines (corresponding frequencies of select data points annotated). Here fit is shown for coordinate number $N=3$ (similar results for other $N$). Figure published in [96].
capacitive (e.g. non-Faradaic) window for EIS experiments. We then conducted potentiostatic testing to determine the capacitance of each sample. We applied a square wave, with a positive potential varying from 0.05 to 0.5 V, discharged at 0 V vs Ag/AgCl for 2 minutes while the current response was measured and subsequently integrated to calculate charge. From measuring charge as a function of voltage, we determined the steady state capacitance and normalized by the total CNT surface area to determine $C_{dl}$. Finally, we conducted EIS measurements at half-cell voltages between 0 and 0.5 V vs. Ag/AgCl to study the frequency response between 10 kHz to 100 mHz of the VA-CNT electrodes.

2.3 Electrochemical Results and Discussion

We used three-electrode measurements to analyze the $C_{dl}$ and frequency response of the electrodes. We then used a modified porous distribution model described here to extract values for the mean and dispersion of the inter-CNT spacings in varying density VA-CNT forests. CV scans at 10 mV/s showed that VA-CNT electrodes behave capacitively from -0.5 to 0.5 V vs. Ag/AgCl (figure 2-3(a)). The volumetric capacitance of the electrodes scales with the density of the CNTs, from 0.47 F/cm$^3$ at $V_f = 1\%$ up to 8.1 F/cm$^3$ at $V_f = 15.8\%$. This result indicates that while increasing densification of the carpets, the gravimetric capacitance is maintained. The $C_{dl}$ varied between 7-12 $\mu$F/cm$^2$ (figure 2-3(b)), independent of volume fraction. These values are comparable to double layer capacitances in literature ranging from 6-50 $\mu$F/cm$^2$ [70, 98, 71, 72, 73, 99, 69]. The capacitance values measured here imply that a 100% efficient two-electrode CDI cell comprised of VA-CNTs operating at 1V could have upto 6.6-10.5 mg salt adsorption/g electrode material. The Nyquist plot (figure 2-3(c)) shows the impedance response for varying volume fractions from 1-15%. The high frequency response has the 45° slope, characteristic of porous electrodes [83]. In addition, the impedance increases with higher volume fraction as expected from the increasing ionic resistance with a smaller $\Gamma$. In the low frequency regime, the impedance slope tends toward a value < 90°, suggesting that there is a sizable
2.4 Porosimetry Analysis

To use the electrochemical measurements to determine the morphology of the VA-CNT carpets, we extended de Levie’s transmission line model for porous electrodes [83], through which EIS can be used to analyze the pore structure. In the de Levie model, an applied sinusoidal potential with frequency \( \omega \) across a single cylindrical pore, generates an electrical impedance response, \( Z_p \), given as

\[
Z_p = \frac{1}{\pi \sqrt{(2 \kappa r^3 \omega C_{dl})}} \coth l_p \sqrt{\frac{2 j \omega C_{dl}}{\kappa r}}
\]  

(2.1)

where \( r \) is the radius, \( l_p \) is the pore length, capacitance \( C \), in an electrolyte with conductivity \( \kappa \), and the double layer capacitance \( C_{dl} = C/A_{pore} \) where \( A_{pore} \) is the electrode surface area of the pore. Due to the known variations of \( C_{dl} \) in carbon materials which is dependent on surface chemistry, crystal structure, and electrolyte [67], it is essential to obtain an experimentally characterized value rather than literature values. In this model, we assume that the CNT resistivity is negligible because the resistivity of electrolyte in the pore is much higher. For a porous electrode with \( n \) uniform pores, the total impedance is then simply \( Z = Z_p/n \). However, a system that has a distribution of pore sizes will have a non-uniform impedance response [100]. The total impedance response, \( Z_{tot} \), for a porous electrode with a distribution of radii given by a mean radius \( \mu_r \) and dispersion \( \sigma_r \) described by a probability density function \( f_{pdf} \) [100] is

\[
Z_{tot} = \left( n \int_{0}^{\infty} f_{pdf}(r_o : \mu_r, \sigma_r) d(r_o) \right)^{-1}
\]  

(2.2)

In this treatment, there are three free parameters: \( \mu_r, \sigma_r, \) and \( n \), and it has been shown that this leads to many possible solutions due to the ability to vary both the total pore volume and \( \sigma_r \) for a given \( \mu_r \) [101]. For many porous electrode materials such as activated carbon where the total number of pores is unknown, this

variation of \( \Gamma \) in the forest [100].
Table 2.1: Converting cylindrical pore geometry to coordinate morphology. In the schematics, the blue area is the wetted region confined by the red-dashed lines, defining the pore, and the gray circles are the CNTs added to show clarity.

can lead to an infinite number of solutions [102]. However, in the case of any brush electrode, where the total number of wires can be calculated based on mass, we can determine \( n \) by assuming a coordination geometry. Previous work [92] suggests that the coordination of the VA-CNT forests can range from hexagonal packing with defects to cubic, pentagonal, or ideal hexagonal packing, with coordination numbers \( N = 3, 4, 5, 6 \) respectively (figure 2-1(b)), and a corresponding number of CNTs per pore, \( M_{\text{cnt}}(N) \). Therefore, by assuming \( N \) for the VA-CNT forest, we can calculate the total number of pores, \( n \), by dividing the number of CNTs by \( M_{\text{cnt}}(N) \), and eliminate \( n \) as a free parameter. Finally, in order to properly represent VA-CNT forests as cylindrical pores given in equation (2.2), we projected the cross-sectional area of the pore and the double layer capacitance from a coordinate morphology to a cylindrical pore.

We convert de Levie’s cylindrical pore model [83] to a corresponding coordinate morphology for pillar arrays by projecting top-view equivalent cross sectional areas \( A_x \) and electrode surface area per unit cell \( A_{\text{pore}} \). For a given radius \( r \), coordinate number \( N \), and pillar diameter \( d_o \) we equate the cross sectional area of the cylindrical and coordinate morphologies, and solve for the lattice constant, \( a_n \). From \( a_n \) we can calculate the average pore inter-CNT spacing, \( \Gamma \). The derivation of the lattice equations are outlined previously [92]. Table 2.1 outlines the equations used to convert from \( r \) to \( \Gamma \).
After projecting the pore geometry, we can then write the pore double layer capacitance as

\[ C_{\text{dl, pore}} = \frac{C_{\text{dl}} M_{\text{cnt}} A_{\text{cnt}}}{A_{\text{pore}}(r_o)} \]  (2.3)

where \( A_{\text{cnt}} \) is the outer surface area of an average CNT. Therefore, the impedance response and subsequently the calculated inter-CNT spacing are dependent on the CNT outer diameter, which has also been shown in theoretical analysis [92]. While previous VA-CNT porosimetry work has assumed \( M_{\text{cnt}} = 1 \) [69], the coordinate analysis suggests that \( M_{\text{cnt}} \) varies between 1.5 to 3. This result indicates that the CNT densities were overestimated in the earlier work. Porosimetry was obtained in this study using equation (2.2) where four possible \( N \) values were used to establish the range of possible interspacings and to give a more accurate description for varying densities of forests. We selected a Gaussian distribution for \( f_{\text{pdf}} \), based on the interspacings characterized at high volume fractions from past work with BET [103], solute rejection [91] and stochastic modeling [93]. We used the \( C_{\text{dl}} \) measured from potentiostatic testing as an input for each sample when conducting the porosimetry analysis.

2.4.1 Porosimetry Results, 1M NaCl

The modified transmission line model given in equation 2.2 was used to first calculate the mean and dispersion of radii if the CNTs were modeled as cylindrical pores. A characteristic length that can be used to estimate charging time constants of capacitors is the pore volume to surface area, \( h_p \). For a cylindrical pore \( h_p = r/2 \). This value can help give insight into the electrode porous properties. This volume-to-area ratio is plotted against volume fraction in Figure 2-4. We compare the results to an idealized cell packing of straight cylinders with \( N=3 \). Straight pillar packing alone over-predicts the interspacing suggesting that waviness may be important to modeling the inter-CNT spacing from theory.

We convert the pore volume to surface ratio of the pore given in Figure 2-4 to a packing morphology to calculate \( \Gamma \). Given that \( N \) is a fitting parameter, we first look
Figure 2-4: Pore volume to surface area calculated from impedance spectra. Markers are experimental data and solid lines are calculated from idealized cell packing \[93\]. Vertical error bars are the dispersion of the radii calculated from the transmission line model.

at the results for all coordinate numbers given in Figure 2-5 and 2-6. For comparison, we also plot the results of a stochastic CNT model \[93\], where CNT growth is simulated for a given $N$ and $w$ to account for non-idealities in the forest. It seems that there is likely a mixture of coordination numbers in a given sample so that the calculated interspacing is somewhat lower than the model predictions for a given $N$. Regardless of coordination number, waviness $w$ tends to be reduced with higher volume fractions, though at high volume fractions we see an increase in $w$ again.

### 2.4.2 Porosimetry Summary in 1M NaCl

Given that $N$ is a fitting parameter, we analyze the upper and lower bound cases of $N = 3$ and $N = 6$ for the value of $\Gamma\mu$, given in Figure 2-7. For comparison, we also plot the results of a stochastic CNT model \[93\], where CNT growth is simulated for a given $N$ and $w$ to account for non-idealities in the forest. The as-grown 1% $V_f$ forests have a $\Gamma$ of 77-110 nm with a $\sigma$ of 40-60 nm. As the samples were densified to 26% $V_f$, $\Gamma$ was reduced to 9-15 nm with $\sigma$ of 4-5 nm. The average inter-CNT spacing decreased with densification, but also the sample uniformity increased. At low $V_f$,
Figure 2-5: Mean nanowire interspacing calculated for given coordinate numbers: a) N=3, b) N=4, c) N=5, d) N=6. Markers are experimental data and solid lines are calculated from a previous model \cite{93}. Vertical error bars are uncertainty in mathematical analysis. As the coordination number increases, the model’s calculated inter-spacing decreases. Higher volume fractions tend to match models for higher coordinate numbers.
Figure 2-6: Standard deviation of nanowire interspacing calculated for given coordinate numbers: a) N=3, b) N=4, c) N=5, d) N=6. Markers are experimental data and contours are calculated from a previous model based on a prescribed waviness $w$ [93]. Vertical error bars are uncertainty in porosimetry analysis. As the coordination number increases, the model’s calculated dispersion decreases. Higher volume fractions tend to have less wavy CNTs.
\( \sigma \) was very large, suggesting that there is not a strong packing coordination in the forest, and there is high dispersion in the nanotube \( \Gamma \)'s which is also consistent with the large spatial inhomogeneities recently observed using 3D quantitative electron tomography [102]. At higher \( V_f \), the array tends towards hexagonal packing when compared to the stochastic model [93] though the dispersion is such that the sample likely had a mixture of packing order. The stochastic model trend diverged from the impedance results with higher \( V_f \), which may be due to bundling or buckling of CNTs during the densification process, leading to greater inhomogeneities. When comparing these results to previous SEM characterizations [92], we found that the EIS approach predicted larger \( \Gamma \) and \( \sigma \) of the interspacing than what was observed optically in a 2D image. This discrepancy may be due to the electrochemical approach providing measurements over the entire forest rather than a cross-section, or that the waviness of the CNT samples lead to a larger standard deviation in spacings than what can be measured optically. The results suggest that a bulk measurement such as this impedance approach is more comprehensive.

Finally, we compared the dispersion calculated in the impedance analysis to stochastic modeling of CNTs with a specified waviness. Figure 2-7(b) shows that the impedance analysis predicts a large \( \sigma \) of the VA-CNT array at low \( V_f \) and it tends to decrease with increasing \( V_f \). The agreement between calculated \( \sigma \) and stochastic model [93], suggests this trend may be due to decreasing waviness of CNTs in the forest. These observations are also in line with qualitative observations made from SEM imaging in figure 2-1(a), and quantified recently by other groups [104]. However, at very high densification, we observed a deviation from this trend, which indicates that there may be other effects (such as buckling) that can contribute towards higher tortuosity. Accordingly, for sparse VA-CNT electrochemical devices, it can be important to model the electrode as having a distribution of interspacings due to the waviness of the CNTs, in order to accurately predict the power density. However, at high \( V_f \) (>15\%), waviness effects may be negligible, and the system can be modeled more similarly to pillars, assuming that there are no other inhomogeneities in the forest. In addition, the porosimetry results derived here can be used to predict
Figure 2-7: Inter-CNT spacings of VA-CNT forests compared to stochastic model [93]. a) $\Gamma$ calculated from EIS and compared to theory given by solid lines [93]. Data shown for $N=3$ and $N=6$ fittings (points are average $\Gamma_\mu$, vertical error bars represent the dispersion $\sigma$). Gray region shows span of $\Gamma$s for $N=3$ to $N=6$. b) $\sigma$ for varying volume fractions. Contours depict waviness, $w$, of CNTs, calculated from the model [93]. Plot shown here for $N=3$ (similar plots in supplementary material for $N=4,5,6$). Vertical error bars are uncertainty of $\sigma$ in porosimetry analysis. Figure published in [96].
the power performance of similar electrodes in other concentrations and species of electrolytes. This analysis can extend a simple beaker supercapacitor experiment to modeling the performance of batteries, fuel cells and desalination devices with more complex kinetics based on the geometries ascertained *via* EIS and transmission line models.

### 2.5 Experimental Results in 500 mM NaCl Electrolyte

To further validate the experimental approach, we performed experiments in two solutions to vary conductivity and its role on the frequency response in the measurement. Below, we show additional experimental results from 500 mM NaCl. The $\Gamma_\mu$ and $\sigma$ are consistent with the 1 M NaCl results, suggesting the robustness of our characterization technique. First, we conducted the potentiostat measurements (Fig 2-8). Due to the decreased solution concentration, the capacitance is slightly reduced from the 1M results from 7-12 $\mu$F/cm$^2$ to 5-8 $\mu$F/cm$^2$. In addition, as expected, the impedance spectra (Fig. 2-8c) has a higher resistance due to the decreased conductivity of the solution. Porosimetry analysis of these experiments yielded similar results to the 1 M NaCl experiments (Fig 2-9). The relative difference between 1 M and 500 mM NaCl sample analysis was 5% for $\Gamma_\mu$ and 15% for $\sigma$.

### 2.6 Conclusions

In this chapter, we characterized the VA-CNT forests using cyclic voltammetry, potentiostatic testing, and impedance spectroscopy. We found that the capacitance was between 22-35 F/g for forests, translating to 6.5-10 mg/g salt adsorption in two-electrode CDI cell operating at 1V. In addition we demonstrated a novel *in situ*, non-destructive method to characterizing nanowire-interspacing using EIS. We showed through careful analysis of electrochemical techniques we can obtain information on $\Gamma$ and $\sigma$ of electrodes based on the response in simple beaker experiments. Our results showed that densified carpets have increased volumetric capacitance and in-
Figure 2-8: Electrochemical characterizations, 500 mM NaCl. a) Cyclic voltammograms (10 mV/s) indicating a capacitance window from 0 to 0.5 V vs Ag/AgCl. b) DC charge vs potential shows that sample capacitance varies between 5-8 μF/cm². c) Nyquist plot of EIS data and model at 0 ± 5 mV. Data in colored symbols compared to the porosimetry model fit (equation 2 main text) given by open symbols and black lines (corresponding frequencies of select data points annotated). Here fit is shown for coordinate number N=3 (similar results for other N).
Figure 2-9: Inter-CNT spacings of VA-CNT forests compared to stochastic model [93], 500 mM NaCl. a) $\Gamma$ calculated from EIS and compared to theory given by solid lines [93]. Data shown for N=3 and N=6 fittings (points are average $\Gamma$, vertical error bars represent the dispersion $\sigma$). Gray region shows span of $\Gamma$'s for N=3 to N=6. b) $\sigma$ for varying volume fractions. Contours depict waviness, $w$, of CNTs, calculated from the model [93]. Plot shown here for N=3. Vertical error bars are uncertainty of $\sigma$ in porosimetry analysis.
creased CNT alignment, which can enhance the overall performance of a VA-CNT electrode. This technique can be used to complement electrochemical investigations to correlate experimental findings with physical modeling.

The work in this chapter is published \cite{96} and available online at \url{https://doi.org/10.1088/1361-6528/aa53aa}. 
Chapter 3

Flow-between Capacitive Deionization Using VA-CNT Electrodes

3.1 Overview

In this chapter, we discuss the design and study of a flow-between capacitive deionization (CDI) system comprised of vertically-aligned carbon nanotube (VA-CNT) electrodes. First, we will discuss the system set up and experimental methodology. Then we will look at results from early prototypes and iterations. Finally, we will explore varying the electrode properties including electrode thickness, density, and surface chemistry to study its effect on desalination.

3.2 Experimental Set-Up

3.2.1 CNT Synthesis and Electrode Preparation

We grew VA-CNT forests using similar recipes outlined in Chapter 2 and described in detail in Appendix [B]. For most of the forests used in this chapter, only the growth time was varied to yield different CNT heights. Standard chemical vapor deposition
of ethylene yields growth of VA-CNTs on iron catalysts on silicon wafers. In the final step of the growth, oxygen or steam is bubbled through the furnace to etch amorphous carbon and allow for easy delamination.

We measured the heights of the carpet, $l$, using SEM (Merlin, Zeiss) and optical microscopy (Axiotech, Zeiss). In addition, Raman spectroscopy, thermogravimetric analysis (TGA), transmission electron microscopy (TEM)(Tecnai, FEI) were used to characterize the quality of the nanotubes. Following delamination from the substrate, we measured the mass, $m$, using a microbalance (Discovery, Ohaus). The electrode volume was calculated as the growth wafer area multiplied by the height of the forest. Finally, in order to strengthen the CNT film and reduce contact resistance, we sputtered 20 nm of Ti and 200 nm of Pt on the bottom of the forest. We previously considered gold-gold self-diffusion [6], but found the introduction of gold to the system limited the voltage window of the CDI cell as given by the standard reduction potential below.

$$\text{AuCl}_4^- + 3 e^- \leftrightarrow \text{Au}(s) + 4 \text{Cl}^- \quad [+0.93 \text{ V}] \quad (3.1)$$

If a cell is driven up to 2V, corrosion can result.

The VA-CNT delaminated film was then mounted against a titanium metal current collector. In the first and second prototype, the film was simply constrained using a PEEK mesh either bolted or epoxied in place. In the third prototype, we also introduced carbon tape (3M) on the Ti current collector for a stronger, flatter mount. An example half cell is shown in Figure 3-1. Finally, the two half cells are mounted together to form a two electrode CDI cell.
3.3 Flow-between CDI System Set Up

We chose a flow-between CDI cell set up due to simplicity of modeling its boundary conditions. In this section we will outline the process for initializing the system, how measurements are made, and finally the calculations made to study the characteristic metrics of the flow cell prototypes.

3.3.1 Fluid Line Set Up

In literature, researchers have chosen to either operate the cell in batch or single-pass modes \[105\]. In a batch-mode experiment, the effluent is recycled back into the inlet. This can be useful in practice, especially in small-scale applications, for converting a known volume of water to a final known concentration in the system. However, in batch-mode experiments the inlet concentration varies with time, which can change the base charging dynamics of the system. In a single-pass system the inlet concentration, \(c_\infty\), is constant, so that the boundary conditions are invariant. As a result, kinetics are simplified, as the optimal flow rate and charging time does not vary over a cycle (mass transport resistance increases with low salt concentration).

In this experiment we use a single pass mode of operation as shown in Figure 3-2. We used a peristaltic pump (Masterflex, Cole-Parmer) for flows greater than 0.06 mL/min. We used a syringe pump (Harvard Microfluidics) for flows that are slower.

3.3.2 Flow Cell Initialization

First, the NaCl solution was deaerated in order to minimize oxidation of the electrodes \[106, 64\]. We flowed He(g) into the inlet reservoir in order to displace any oxygen dissolved in the water. Then, once the flow cell was plugged into the system, we introduced liquid into the electrode by flowing a low-surface tension fluid through the cell. Water has a surface tension of 72 dynes/cm, while isopropanol (IPA) and 0.2 mM Triton-X 100 have surface tensions of 23 and 30 dynes/cm, respectively. We flowed the low surface tension fluid first, in order to ensure the void space of the electrode was fully wetted. In early prototypes we used IPA, but in the final prototype
configuration we used 0.2 mM triton-x 100 due to the chemical incompatibility of IPA and acrylic tape. The initial low-surface-tension fluid flowed through the cell for 20 minutes at a rate of 1 mL/min. Then, the inlet fluid was gradually exchanged with NaCl solution by partially opening the valve to the salt solution and partially closing the solvent tank. Ultimately, over a period of 20 minutes, the low surface tension fluid was completely exchanged to NaCl. Finally, NaCl continued flowing to prime the system until the conductivity probes at the inlet and outlet read stable values corresponding to the bulk concentration.

In addition, for all experiments, data was analyzed after the first 3-5 cycles or once the system had reached steady-state cycling. This was because the initial cycle may have higher desalination due to the initial adsorption of ions that may not have completely adsorbed/desorbed in subsequent cycles. By analyzing later cycles, we give a more accurate description of the electrode capacity [64].

Finally, experiments were conducted in 1 mM and 5 mM NaCl. Previous work has shown that 5-50 mM NaCl is the optimal range, because under 1 mM as the local concentration goes to zero, there will be very high resistance. Thus the salt adsorption in 1 mM NaCl will be slower and lower than experiments run in higher concentrations [64]. However, we found that 1 mM NaCl experiments gave us significantly larger
signal in the conductivity probes, so in order to take accurate measurements we were unable to increase the salinity of the feed solution. Thus, we expect our reported salt adsorption results are conservative for VA-CNT electrodes.

3.3.3 Conductivity Measurements

Conductivity, $\kappa$, measurements were made using a flow-through conductivity probe (Edaq, ET917) with a volume of 17 $\mu$L and a meter (Edaq, EP357). The probes were calibrated using the inlet solution, 1 mM NaCl, corresponding to $\kappa = 118 \mu S/cm$ which was calculated using the Aqion software for a room temperature of 22 $^\circ$C. The temperature for calibration was adjusted depending on the season given that the lab averages between 18-23 $^\circ$C depending on heating or cooling systems.

The measured conductivity, $\kappa$ in the experiment is then back calculated to concentration, $[\text{NaCl}]$, (in mM) using the Nernst-Einstein relation for ion conductance:

$$\kappa = \gamma \frac{zF^2}{RT} (D_{\text{Na}} + D_{\text{Cl}})[\text{NaCl}]$$

where $F$ is Faraday’s constant, $T$ is temperature, $R$ is the gas constant, $\gamma$ is the activity constant (10 for NaCl,) and $D$ are ion diffusivities. Example effluent concentration profiles under applied voltages are shown in Figure 3-3.

3.3.4 Voltage and Current Electronics

An Agilent 3000 power supply was used to source voltage and current to the CDI system. A LabJack T7 Pro connected to LabView was used to control the voltage amplitude and duty cycle, as well as measure the current response. These were controlled and measured through several op-amp circuits as outlined in Figure 3-4. Invertible op-amps (TLV4112, Texas Instruments) and power supplies were used in order to measure both positive and negative current responses.

The flow-by cell was operated in constant voltage mode, with cell voltages ranging from 0.5-2V. However, at high voltages we have to be wary of electrolysis and carbon...
Figure 3-3: Example measurements of the CDI Cell (Prototype 2). Here the voltage was varied and the flow rate from 2 mL/min (blue) to 1 mL/min (red).
redox reactions [110]:

\[ \text{C(s) + H}_2\text{O} \rightleftharpoons \text{CO + 2H}^+ + 2e^- \quad [0.52 \text{ V}] \quad (3.3) \]

\[ \text{CO + H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{H}^+ + 2e^- \quad [-0.103 \text{ V}] \quad (3.4) \]

\[ \text{O}_2(\text{g}) + 4\text{H}^+ + 4e \rightleftharpoons 2\text{H}_2\text{O} \quad [1.23 \text{ V}] \quad (3.5) \]

Oxidation can be minimized in the system by degassing the solution, which was done using helium bubbling. The effect of redox reactions in the system can be characterized by studying samples under XPS, but in order to measure fluctuations in pH, a pH probe at the outlet would be best (Appendix A). A preliminary XPS analysis of electrodes following desalination showed increased oxygen content, even in the presence of degassed solution, suggesting that water and existing functional groups on the surface may be reacting.

### 3.3.5 Other Sensors and Future Additions

In addition to conductivity probes, the set up had a thermocouple outside the fluid line to track long-term fluctuations in room temperature. This is important because a 1 °C in temperature change can yield 2% error in accuracy of the conductivity probes.
The temperature fluctuations are tracked and adjusted in the final conductivity to concentration calculations.

Also, in the previous section we mentioned that tracking changes in individual ion concentration could give greater insight into the products of the desalination process in the CDI cell at a given voltage. Previous work has suggested that measuring pH fluctuations can give insight into redox reactions on the electrode surface [106]. We investigated the use of sodium, chloride, and pH probes but found that a ground loop current may have made the measurements unsuitable for analysis (Appendix A). In these studies, we focus on conductivity measurements alone, but we recommend continuing to explore measuring ions in the system for more accuracy and insight. It is possible that inductively coupled plasma atomic emission spectroscopy (ICP-AES) could achieve this, but it is a cost-prohibitive approach. Further details are given in Appendix A.

### 3.3.6 Electrode Measurements and Characterizations

The key metrics for a CDI device are the electric charge, the salt adsorption, the salt adsorption rate, and the charge efficiency[64]. The approach for determining these metrics through charge-discharge cycling (for adsorption and electrochemical cells) was proposed first by Oren, Soffer and Folman [20, 111]. These parameters can be used to understand the performance of the electrode and device with respect to other existing materials.

We can use the measurements taken by our set-up such as those given in Figure 3-3 to determine these metrics. The charge, $Q$ on the electrode is calculated from the current,$I$, response.

$$Q = \int I dt$$ (3.6)

The coulombic charge can be converted to moles by dividing by Faraday’s constant.

$$Q_{mol} = \frac{Q}{F}$$ (3.7)
The salt adsorption, $S_{ads}$ capacity can be calculated through a volumetric conservation of moles by multiplying the flow rate $\Phi$ with the integrated change in effluent concentration.

$$S_{ads} = \Phi \int c_{out} - c_\infty dt$$ (3.8)

However, because conductivity probes are more accurate with differential measurements we use $S_{ads} = \Phi \int c_{out} - c_{out}(t = 0) dt$ and use the inlet conductivity probe to verify that the inlet concentration is constant. Generally, the salt adsorption is normalized by the mass of both electrodes when they are dry [112].

The salt adsorption rate, $S_{rate}$ is simply $S_{ads}$ divided by the cycle time. We determined $\Delta t_{cycle}$ to be the time when cumulative salt adsorption or desorption is greater than 90% of the final value.

$$S_{rate} = \frac{S_{ads}}{\Delta t_{cycle}}$$ (3.9)

While the salt adsorption rate has only been looked at in detail by a few groups [105, 113], it can be important for understanding optimal water desalination in operation. Recently, a Ragone-style plot comparing $S_{ads}$ and $S_{rate}$ was developed by Kim and Yoon [66]. While the salt adsorption rate is dependent on the electrode porosity, other system parameters such as operating flow rate can significantly swing this measurement.

Finally, charge efficiency, $\eta$, is a ratio of the moles of electric charge that is used to charge/discharge the device compared to the moles of salt removed from the solution [116, 114, 115]. $\eta$ can be used to determine short-comings in salt removal due to leakage currents, Faradaic reactions, redox reactions on the carbon surface, or charging resistance. Generally, increasing voltage applied across the cell increases charge efficiency [116, 117].

$$\eta = \frac{Q_{mol}}{S_{ads}}$$ (3.10)
3.4 First and Second Prototype

In this work, the design of early CDI cell designs was based on a preliminary scaling analysis from beaker experiments. In Chapter 2, we determined the capacitance of VA-CNTs in NaCl to vary between 22-35 F/g or 0.75-1.19 F/cm$^3$. For 1 F/cm$^3$ (normalized by two electrodes), this would yield a salt adsorption of 5 mM. Thus, a small cell with an inlet concentration of 1 mM could have strong, measurable changes in effluent concentration. However, experiments with the first prototype showed that capacitance and electrode salt adsorption were much lower than anticipated from beaker experiments. Therefore, the second prototype used a larger volume electrode, in order to increase signal.

The first prototype cell started with an electrode size of 4 x 1 x 0.1 cm (Figure 3-5). The CNT electrodes were constrained against a titanium current collector with a PEEK mesh epoxied to the metal. A shim of 380 $\mu$m provided a gap between the electrodes, the space in the channel for fluid to flow. The ports were placed 1 cm on either side of the electrode, to allow for sufficient length to take care of any flow entrance effects.

Preliminary experiments were run with the first prototype, varying the solution flow rate to determine an optimal experimental condition for quick but measurable salt adsorption capacity (Figure 3-6). We found that a flow rate between >1 mL/min yielded the largest salt adsorption in the cell. This variation in salt adsorption measurements could be due to the sensitivity of the conductivity measurement. Long time scales for charging at low flow rates may not be captured. In addition, there may be degradation over testing, which will be discussed in greater detail next.
Transitioning from the first prototype to the second prototype, the cell electrode area was increased to 2 x 8 x 0.1 cm in order to increase the magnitude of change in the effluent peaks, boosting the overall signal-to-noise in the conductivity measurements.

Finally, experiments were run in both 1 mM and 5 mM NaCl, but the measured VA-CNT salt adsorption in the higher salinity feed was lower (Figure 3-7). While the reason for this is attributed to the unsuspected degradation of the cell, we find in general that the V_{f} 1% CNT electrodes adsorb about 1 mM salt, suggesting that experiments run in 1 mM NaCl will provide the best signal for characterization.

The salt adsorption measured in the initial cells was lower than anticipated (0-4 mg/g in Figure 3-6). Charge efficiency suggests that possibly the surface chemistry is influencing the performance of the electrode. In the next section, we will explore limitations of the VA-CNT electrodes and possible degradation mechanisms.

### 3.4.1 Investigating Cell Degradation and Capacitance Variance

Degradation of carbon is evident in most CDI systems. It is believed that carbonic acid formation degrades the carbon surface [110]. The second prototype cell tested at a constant voltage of 2 V over 24 hours showed reduction in the effluent concentra-
Figure 3-7: Salt adsorption in 1 and 5 mM NaCl solutions. Higher inlet concentration showed reduced charge efficiency and salt adsorption capacity.

The point of zero charge (PZC) is defined as the voltage at which the surface charge is neutral. This potential exists because all surfaces have some non-specific adsorption which occurs when dipped in electrolyte [19]. Generally, carbon materials have some functional groups on the surface which will result in a non-zero PZC. The PZC of a material can be determined through beaker experiments, by measuring the differential capacitance over varying potentials [119].

PZC analysis of samples pre- and post-beaker experiments were conducted by
calculating the differential capacitance for varying applied voltages using impedance spectroscopy. At low frequencies, the impedance response is purely imaginary and 
\[ C = \frac{1}{\omega Z''}. \]
The voltage that gives the minimum capacitance is roughly the PZC. For VA-CNTs exposed to 1V vs Ag/AgCl over 24 hours resulted in a PZC shift from -0.2 to +0.1V (Figure 3-8b). Preliminary XPS of samples was conducted, but the results of increasing oxygen were not statically significant different between electrodes tested at varying voltages. Further testing will be needed to determine if oxidation is occurring during high voltage charging.

In addition to changes in surface chemistry, we considered whether synthesis of the VA-CNTs created variability in the capacitance or quality of the carbon. The quality here is simply a measure of the presence of amorphous carbon. Thermogravimetric analysis (TGA) of VA-CNTs in air was used to study the combustion temperature of the CNTs (Figure 3-9). The TGA was ramped to 800 °C at a rate of 5 °C/min. The degradation temperature was \( \sim 690 \) °C, which suggests most of the carbon is highly ordered graphitic sheets \[ 120 \]. Follow up imaging with TEM (Figure 3-9), also showed some presence of amorphous carbon on the surface. The Raman spectra was also used to understand the quality of the CNTs by studying the surface response at 1200-
Figure 3-9: Analysis of amorphous carbon on VA-CNT electrodes. a) TEM imaging shows some amorphous carbon on surface while b) the TGA analysis suggests that overall the CNTs are very high quality, degrading at 690 °C.

2000/cm wavelengths (Figure 3-10a). Raman can provide insight into the ordering of the nanotubes as well as surface functional groups [121], especially when looking at the D and G bands [122, 120]. Graphene, without the presence of amorphous carbon will have a high intensity G band, $I_G$, and a low intensity D band, $I_D$. By measuring the Raman spectra, and calculating the ratio $I_D/I_G$, a qualitative estimate of the carbon nanotube structure can be conducted. The lower the ratio, the higher the quality of the VA-CNTs. We used beaker experiments, similar to the procedure outlined in Chapter 2, to compare capacitance and the $I_G/I_D$ band ratio. We found only a slight correlation between Raman spectra and capacitance (Figure 3-10b). In addition, the capacitance of an electrode was compared with its position and order in batch processing. While there is still variability of the capacitance between 20-40 F/g, there does not seem to be a strong dependence on the location of wafers in the furnace and the processed batch order (Figure 3-10c).

In summary, while the origin for varying capacitance is unknown, it seems that a shifting PZC is indicative of cell degradation. Thus, reducing the PZC shift of the electrode will be important to longterm stability. This is likely true for many carbon electrodes tested, and something that will require thoughtful engineering. Further testing will be needed to determine the source of these fluctuations and stabilize them.
3.5 Third Prototype

For the third prototype, 2 x 8 cm planar area VA-CNT forests were used of varying heights and densities. In order to assess the best-case salt adsorption capacity, we used fresh electrodes tested at a single voltage. This minimized the effects of aging on calculating $S_{ads}$. Devices were tested at flow rates of 2 mL/min with 1 mM inlet concentration for all experiments. An example half cell is shown in Figure 3-1.

3.5.1 Voltage Dependence Results

Voltage-dependence studies of VA-CNT forests were conducted with $l_e = 800 \mu$m. The voltage was varied between 0.75-2.0 V, and the outlet concentration as well as the current response were measured. The data in this section is normalized by the total carbon mass in the cell. The effluent profiles are shown in Figure 3-11. While similar cycle times are observed across different voltages, the peaks increase in amplitude with increasing voltage. The characteristic calculations of the electrode
Figure 3-11: Outlet concentration profiles of V₁ 1% CNTs tested at varying voltages. The capacitance of the cell was measured as the slope of the charge vs voltage. The capacitance was calculated as 10 F/g, which is similar to values measured in beaker experiments in Chapter 2 (22-35 F/g single electrode), though it is on the low-end of what was anticipated. However, the capacitance will be lower in a CDI cell operating at 1 mM NaCl vs beaker experiments conducted at 1 M NaCl due to the increased Debye length and resistances in the electrode. The maximum salt adsorption observed is 5.5 mg/g at 2 V at a rate of 0.3 mg/g-min. The charge efficiency asymptotes to 60% suggesting that the presence of leakage currents, Faradaic reactions, and co-ion desorption before counter-ion adsorption could all play a role in reducing the overall electrode capacity.

3.5.2 Electrode Thickness Results

In order to increase the kinetics of desalination, the thickness of the CNT forests was reduced from \( l_e = 800 \) to \( l_e = 450 \) μm. The cells were tested at 2 V, using a flow rate of 2 mL/min. The effluent profiles shown in Figure 3-13 indicate that the desalination curves do appear to have a shorter charging and discharging period. Figure 3-14 shows the calculated characteristic parameters of the cell. The gravimetric charge was comparable between the two cells, roughly 22 C/g. However the observed salt adsorption of the thin electrode was greater, at 8 mg/g. This increase may
Figure 3-12: CDI cell performance for varying operating cell voltages. All electrodes are $V_f 1\%$, with $l_e = 800\mu m$. 
be due to variation in the quality of CNTs or in the assembly of the electrode and cell. In addition, it is possible that the faster charging kinetics can allow for greater resolution of conductivity changes and therefore a more accurate $S_{ads}$. A fully charged $l_e = 800 \, \mu m$ electrode could take over one hour versus the $l_e = 400 \, \mu m$ only requiring twenty minutes, as shown in Figure 3-13. In the former case, it is difficult to measure conductivity changes in the tail during the final charging. The salt adsorption rate was improved significantly from <0.1 mg/g-min to 0.35 mg/g-min. This was a 3-4x increase in salt removal rate for a reduction of 45% electrode thickness. This increase is in agreement with the rate anticipated by looking at the electrode diffusion time scale, $\tau_d = l_e^2/D_{NaCl}$, which suggests a 3.2x increase in the rate of desalination between these two systems. This suggests that the desalination is diffusion-dominated, and reducing electrode thickness will directly impact the desalination time scale.

### 3.5.3 Electrode Density Results

Because sparse CNTs only remove 0.2-0.4 g/cm$^3$, densification can increase the volumetric concentration of salt removed. However, increasing density reduces diffusivity, which can lead to increased rates of salt removal. Here, we synthesized denser VA-CNT forests by varying the partial pressure of gases during growth, yielding electrodes that are 5x denser than the sparse forests used previously.
Figure 3-14: CDI cell performance for two electrode thicknesses $l_e$. Forests are $V_t$ 1% and have an operating cell voltage 2V. The salt adsorption and gravimetric charge are similar, but the rate of desalination is improved by 3-4x, consistent with a change in the electrode diffusion time scale.
Figure 3-15: Outlet concentration profiles of $V_f$ 1% CNTs and $V_f$ 5% of comparable height.

In Figures 3-15 and 3-16, we compare the 1% $V_f$ forests to 5% $V_f$. As anticipated, the effluent salt concentration shows slower desalination rates for the 5% $V_f$ system. The gravimetric charge was similar, though the salt adsorption was slightly reduced for similar reasons discussed in the previous subsection. The desalination rate was slightly reduced though the effect is not as dramatic as it is with the reduction in electrode thickness. A quick look at the diffusion time constant, $\tau_d$, suggests the magnitude is due to the reduced porosity:

$$\tau_d = \frac{L_e^2}{((1 - V_f)D_{NaCl}}$$

$$\frac{\tau_1}{\tau_5} = \frac{(450\mu m)^2/(.99D_{NaCl})}{(400\mu m)^2/.95D_{NaCl}} \sim 1.3$$

A reduction in porosity between these two cells, leads to $V_f$ 1% carpets that are 1.3 times faster than the $V_f$ 5%, which is in agreement with the experimental findings. This suggests that transport in these cells is diffusion-dominated.

### 3.5.4 Chemical Functionalization Through UV-Ozone

In Section 3.4.1, we explained that a shifting PZC can be detrimental to CDI cell performance. However, engineering the surface PZC or selecting an applied potential
Figure 3-16: CDI cell performance for two different electrode densities $V_f$. Electrodes have comparable height (400-450 $\mu$m) and were operated at 2 V. The salt adsorption and gravimetric charge are similar, but the rate of desalination is reduced by 1.3x, consistent with a change in the electrode diffusion time scale.
close to the PZC can be used to maximize CDI electrode salt adsorption [114]. Previous work has shown that the addition of acidic and oxygen functional groups on the surface can increase $S_{\text{ads}}$. This functionalization of carbon can be achieved through nitric acid treatment [123, 124, 125], dip-coating in a polymer [126, 127], or plasma-treatment. In addition, deliberately tuning a PZC to increase the voltage window can allow the device to operate at larger voltages and therefore increase charge and salt removal [128].

In order to maintain the VA-CNT structure, a dry-functionalization method was chosen. UV-Ozone exposure [129] can create C-O functional groups on the surface of the VA-CNTs which can increase surface wettability, capacitance, and shift the point of zero charge (PZC) of the electrode. We showed with 1 hour of exposure to 254 nm wavelength UV (Figure 3-17), the capacitance could be doubled from 20-40 F/g. In addition, the PZC was shifted from -0.1 to +0.2 V vs Ag/AgCl which can help minimize co-ion adsorption by selectively using asymmetric electrodes in the CDI cell. Experiments were run with VA-CNT electrodes where either both the anode and cathode were treated with UV-Ozone, or just the cathode was treated with UV-Ozone (Figure 3-18). Figure 3-19 shows that while adsorption is the same between the cells and comparable to the previously analyzed electrodes, the desalination rate
is much faster in the UV-ozone treated cell, up to 0.6 mg/g-min. It is possible that the shifted PZC allows for minimal co-ion adsorption, thus increasing the overall $S_{\text{rate}}$. However, the additional gains in charge may be pseudo-capacitive, and therefore do not contribute to increasing the net $S_{\text{ads}}$. In addition, both cells still show degradation over long-term cycling. It is possible that greater UV-Ozone treatment operating at lower voltages could operate more stably.

Finally, we conducted some extensive beaker testing of UV-Ozone treated samples in order to determine the optimal UV exposure time for thin, $l_e = 400 \mu m$ electrodes. A short exposure time may not completely functionalize the surface, while a long exposure time may begin to introduce defects to the CNT structure reducing conductivity and ultimately capacitance. For $l_e = 400 \mu m$, beaker experiments showed that 120 minutes under 254 nm UV yielded capacitances 3-4x greater than the baseline capacitance of as-grown VA-CNTs, shown in Figure 3-20.

3.6 Summary

We demonstrated a VA-CNT cell with up to 8 mg/g $S_{\text{ads}}$ with 0.6 mg/g-min $S_{\text{rate}}$, summarized in Figure 3-21. Increasing density and reducing electrode thickness yields
Figure 3-19: CDI cell performance for UV-Ozone treatments comparing an as-grown carpet, an asymmetric set up (UV-Ozone-A), and both electrodes treated under UV (UV-Ozone-B). All forests are $V_f$ 1% with $l_n$ roughly 400 $\mu$m, and operating cell voltage 2 V. The UV-Ozone treated cells have higher gravimetric charge, but similar salt adsorption. The asymmetric cell has a much greater rate of desalination, possibly due to reduced co-ion desorption prior to counter-ion adsorption.
Figure 3-20: VA-CNT capacitance in 50 mM NaCl as a function of UV-Ozone exposure time for CNTs of \( l_e = 400 \mu m \) and 1 x 1 cm area. The capacitance can be increased from 20 to 80 mF suggesting functionalization leads to increased pseudo-capacitance.

desalination times that are proportional to the diffusion time constant. This suggests that thinner electrodes can yield faster desalination rates, while the trade-off with densification is not as strong. The charge efficiencies demonstrated were <60% suggesting that reducing resistances, minimizing corrosion, and increasing operating salt concentrations could improve performance.

In this section, we experimentally explored the salt adsorption capacity of VA-CNT electrodes and improvement methods. However, the rate of desalination is not only dependent on the electrode properties. It can be tuned by considering other device parameters such as flow rate, system volume, electrode thickness, and spacer thickness. In the next section, we develop an electrode agnostic model for optimal CDI performance in a flow-between continuous configuration.
Figure 3-21: Summary of salt adsorption vs salt adsorption rate of CDI cells presented in this chapter.
Chapter 4

Advection-Diffusion Model for Optimization of CDI Cell Design

Much of the experimental focus in CDI research has been on characterizing an electrode material’s salt adsorption capacity and removal rate. However, the metric of salt adsorption rate does not provide a complete picture of desalination performance. For example, one could choose very high flow rates for operating their flow cell and report high salt adsorption rates, with little to no desalination of the flow stream. In order to understand the electrode performance coupled with device performance, it is important to consider the system in terms of desalination metrics. To our knowledge, only two previous studies have looked at desalination performance. Previously, Zhao et al. experimentally examined water recovery for an m-CDI [113, 130], constant current system. Demirer et al. experimentally looked at the trade-off between energy recovery and water recovery [131].

In this study, we considered a typical reverse osmosis metric for desalination device design: salt rejection. The salt rejection, $SR$, is a comparison between the average concentration of the permeate, $\bar{c}_{out}$, and concentration of the feed, $c_\infty$:

$$SR = 1 - \frac{\bar{c}_{out}}{c_\infty}$$  \hspace{1cm} (4.1)

It is typical to run flow-between CDI cells in nearly fully-charging and discharging
cycles, in order to characterize salt adsorption. However, the $SR$ during the charging period (Figure 4-1) reaches its maximum at a time different from the equilibrium charging, $t \neq t_{\text{charge}}$. Demirer et al. previously suggested running CDI cells to the effluent peak for highest desalination, but the maximum salt rejection occurs at a different time. This suggests there is an optimal cycling frequency that may not be $t_{\text{charge}}$ or $t_{\text{peak}}$.

The goal of our modeling efforts was to understand the role of device design specifications (feed concentration, desired effluent concentration, flow rate, volume) on design parameters (electrode type, electrode thickness, channel gap, width, length, etc.), for a continuously operating flow-between CDI system. Finally, we will investigate the role of cycle frequency on achieving maximum salt rejection in a device.

In this chapter, we will outline the modeling efforts of the CDI community. Then, we will discuss a model which is electrode-independent to demonstrate how any system can be optimized for desalination. We use this to recommend how to design a CDI cell for a given specification. Finally, we consider additions to the model to optimize
CDI for desalination in terms of water production and energy consumption.

4.1 Prior Modeling Work

Capacitive deionization is still a young technology with many opportunities for modeling and characterizing the system. Capturing the physics of the system and predicting effluent concentration profiles has been a focus of the research community since "capacitive demineralization" emerged in the 1960s [17, 27]. The goal of many modeling efforts has been focused on physically simulating the electric double layer (EDL) dynamics, limited to a specific experimental set up and electrode material.

The first models were started by Murphy and Caudle [17], who sought to study the effluent concentration profile changes. They used a 1D system, modeling advection of ions through the spacer and using a Bessel function to describe the flux of salt out of bulk solution. While the Bessel function was based on electromigration, it did not capture the dynamics of double layer charging or diffusion in the electrode. Finally, the system required three fitting parameters to experimental data so modeling and prediction was limited to only the device characterized.

Soon after, John Newman et al. developed extensive models for transport in porous electrodes [16, 108, 132]. First, they developed a system of equations for transport using Fick’s laws. The ion species flux, \( N_i \), in a system is a function of migration, diffusion and advection [108]

\[
\begin{align*}
N_i = & -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i \vec{v} \\
& \text{(migration)} \quad \text{(diffusion)} \quad \text{(advection)}
\end{align*}
\]

where \( z \) is species charge, \( u \) is mobility, \( F \) is Faraday’s constant, \( c \) is the concentration, \( \phi \) is the potential, \( D \) is the diffusivity, and \( \vec{v} \) is the advection velocity.

The current, \( I \), carried by the ions is the sum of flux multiplied by coulombic charge.

\[
I = F \Sigma z_i N_i \quad (4.3)
\]

The mass balance is given by considering the net flux in and out, and species
generation of a differential control volume element.

\[
\frac{\partial c}{\partial t} = -\nabla \cdot N_i + R_i \tag{4.4}
\]

Finally, there is always conservation of charge in the overall system (bulk electroneutrality).

\[
\Sigma z_i c_i = 0 \tag{4.5}
\]

These basic transport equations can be modified for use in describing the electrode region by accounting for the void volume of a differential element. The ratio of the void to total volume is the porosity \( \epsilon \). By modifying equation 4.4 and accounting for the porosity we get a macroscopic elemental differential equation [108].

\[
\epsilon \frac{\partial c}{\partial t} = \frac{1}{h_p} j_{\text{in}} - \nabla \cdot N_i \tag{4.6}
\]

where \( h_p \) is the electrode volume to surface area ratio, and \( j_{\text{in}} \) is the species production per surface area electrode.

Equation 4.6 forms the premise for extensive CDI modeling. The focus of characterizing electrode charging in a CDI system has been on how best to describe the \( j_{\text{in}} \) term.

For modeling the desalination in an electrode, Johnson and Newman used a linear transmission line model coupled with the porous electrode theory [16]. However, this assumed that the salt adsorption is only dependent on charge and potential and is indifferent to the varying local salt concentration in the pore.

Many decades later, Johnson and Newman’s model was revisited, incorporating concentration variation in the spacer. Biesheuvel et al. [133] attempted to characterize the polarization layers in the electrodes using EDL theory. However, in order to model transport from the spacer region to the electrode, they introduced a mass transport potential to drive fluid from the bulk to the electrode, instead of diffusion. Their model still assumed that the transport in the electrode would follow a transmission line model with constant concentration in the depth of the electrode, and was
only dependent on charge and potential.

However, shortly after, Biesheuvel and Bazant focused on the transport kinetics from a bulk solution into an electrode and showed that the electrode charging in CDI is highly non-linear [134]. Through the Gouy-Chapman-Stern model, outlined in equations 1.1-1.7, they showed that salt adsorption is not only a function of $\phi$ but also the local concentration $c$. The system they looked at was the porous electrode, where a potential, $\phi_e$, is applied to an electrode immersed in a solution with bulk concentration, $c_\infty$. They model transport in the electrode bulk (within the pores of the electrode but at distances greater than the double layer), and related the flux into the double layer as the reaction term as outlined by Equation 4.6. They assumed quasi-equilibrium EDL charging (GCS is dependent on $c$ and $\phi$, and was fully charged at every time step). The governing equations for the electrode are outlined below. Terms are defined in Table 4.1. The discussion outlined here will use $y$ for the position in the depth of the electrode, and $z$ for the thickness of the double layer.

Ultimately, the goal of the model is to determine the salt adsorption in the cell and the charge in order to determine energy and efficiency of the desalination process. These are calculated based on the ion concentration profiles defined by the GCS equations, based on $\phi(t, y)$ and the local electrode bulk concentration $c(t, y)$ (1.1-1.7). In general, the charge is calculated from the difference of excess positive and
negative ions.

\[ q = ze \int_{\lambda_s}^{\text{bulk}} c_+(z) - c_-(z) \, dz \]  

(4.7)

The salt adsorption is calculated from summing the net excess charge of ions with respect to the bulk concentration.

\[ w = \int_{\lambda_s}^{\text{bulk}} c_+(z) + c_-(z) - 2c(y) \, dz \]  

(4.8)

The concentration profiles for \( c_+ \) and \( c_- \) can then be calculated from the Boltzmann distribution in Equation 1.2 using the potential difference across the diffuse layer, \( \Delta \phi_D \).

The potential drop from the electrode to the pore is equal to the potential drop across a fixed Stern layer and diffuse layer.

\[ \phi_{\text{electrode}} - \phi_{\text{pore}} = \Delta \phi_S + \Delta \phi_D \]  

(4.9)

Finally, Gauss’ law is used to determine the Stern layer potential drop and equate it to the charge stored.

\[ q = -\frac{\Delta \phi_S}{\lambda_s} \lambda_d \]  

(4.10)

where \( \lambda_d \) is the Debye length and \( \lambda_s t \) is the Stern layer thickness usually between 0.3-10 nm, though it can be larger \[135, 136\]. Bazant et al. developed non-dimensional analytical solutions from this analysis for the charge and salt expressions \[137\]:

\[ q^* = -2\sqrt{c^*} \sinh \frac{\Delta \phi_D^*}{2} \]  

(4.11)

\[ w^* = 4\sqrt{c^*} \sinh^2 \frac{\Delta \phi_D^*}{2} \]  

(4.12)

. We refer the reader to the paper for details of the derivation.

The flux of salt and charge from the electrode bulk to the EDL is calculated using the time rate of change.

\[ \frac{dq}{dt} = j_{\text{charge}} \]  

(4.13)
\[
\frac{dw}{dt} = j_{\text{salt}} 
\] (4.14)

The flux of salt from the electrode to the double layer is coupled using Equation 4.6, where \( j_{\text{in}} = j_{\text{salt}} \).

Finally, changes in \( c(y, t) \) and \( \phi(y, t) \) can be related to the diffusion of ions and current in the electrode. The flux of salt is determined using Equation 4.6.

\[
\frac{\epsilon \partial c}{\partial t} = -\frac{1}{h_p} j_{\text{salt}} - \epsilon \nabla \cdot N_i 
\] (4.15)

From conservation, the divergence of the current is proportional to the volumetric flux of charge carried in the pore by ions.

\[
\nabla \cdot i_e = -\epsilon h_p j_{\text{charge}} 
\] (4.16)

From Ohm’s law:

\[
i_e = -\frac{zDF}{RT} c \nabla \phi 
\] (4.17)

The above set of equations uses GCS and Fick’s laws to determine the change in concentration and potential along the length of the electrode over time. This analysis can be used to model desalination and calculate the current and effluent concentration profiles. The main fitting parameters are \( \lambda_s \) and \( h_p \) (for most electrodes though as shown in Chapter 2, it can be calculated for VA-CNTs).

In this system of equations, current and ion transport are tracked using GCS. Gabitto and Tsouris took a similar approach [138] and recovered the above Biesheuvel and Bazant equations. From this model, extensive work has been done to couple electrode dynamics with mass transport [116, 139].

One of the main challenges with classic GCS theory is that it only holds where the double layers are non-overlapping. At low salt concentrations the Debye length can be as large as 10 nm. Many porous electrode materials contain large volumes of micropores that are <2 nm. To account for this discrepancy, the modified-Donnan (mD) model [140] was added to the GCS framework for micropore charging.
first version of the mD model implementation, a micropore concentration separated from the macropores was introduced using a Boltzmann distribution \[ c_{mi} = c \exp (-z_i \Delta \phi_{\text{Donnan}} + \mu_{\text{att}}) \]. The chemical potential, \( \mu_{\text{att}} \), represents the excess from electrostatic ion-ion interactions. In subsequent models, \( \mu_{\text{att}} \) was updated to equal \( E/\varepsilon_{\text{ions,mi}} \) calculated by using images forces between ions and the conductive matrix of the electrode \[141\]. This also eliminated the attractive chemical potential as a fitting parameter. The mD model has been used to extend previous GCS models used in CDI\[142, 143, 117, 144\]. Recently, Hemmatifar et al. extended the mD model to a full, 2D, finite-volume simulation of a CDI cell \[144\].

At present, there has been extensive work on characterizing electrode charging for CDI systems of a specified electrode, operating conditions, and volume. However, recently, a couple models have tried to step back from the electrode kinetic details and examine the mass transport overall. Jande and Kim \[145, 146\] introduced an analytical solution to the effluent concentration over time, using a first-order approximation. Liu et al. used a Langmuir approach to analyze the role of voltage and spacer thickness on CDI electrosorption capacity \[147\]. Perez et al. focused on advection-diffusion in a flow-between CDI geometry. By examining the role of the Péclet number (and therefore the flow rate), they started to examine the role of device geometry on the peak concentration at the effluent \[148\]. However, the desalination to the electrode was modeled as mass transport across a porous boundary layer with no salt adsorption/desorption, which may over-predict cell performance since there is no information about the electrode charging. In contrast, a model for flow-through CDI (flow goes through porous electrodes, or in the same direction of the applied electric field), took the unique approach of using a Heaviside function to model the charging in a diffusion-electromigration analysis only \[105\].

In our model, we used Newman’s approach, but similar to Suss et al. \[105\], we used an empirical first-order approximation for electrode-charging. This approach reduces computation time significantly, and allowed us to run a 2D simulation of a CDI cell focusing on the design parameters of the system, regardless of the chosen electrode material, to determine the key design parameters for desalination.
4.2 Derivation of Advection-Diffusion Model

We modeled a flow cell, looking at the half cell (Figure 4-2), with a flow rate \( \Phi \) (m\(^3\)/s), constant inlet concentration \( c_\infty \) (mol/m\(^3\) or mM) with a half-cell gap of \( L_{sp} \) (total cell gap is \( 2L_{sp} \)), and electrode thickness \( L_e \). The electrode has some porosity \( \epsilon \) and tortuosity \( \tau \), which is accounted for in the term of the effective diffusivity \( D_e = \frac{\epsilon D_{NaCl}}{\tau} \). We tracked the concentration along the spacer channel, \( c(x, t) \), and in the electrode, \( c_e(x, y, t) \). Because \( L_{sp} \ll b \) and \( L_c \gg L_{sp} \) we assumed fully developed, laminar flow in the spacer channel.

In the spacer, we considered the fluxes across a differential control volume element (Figure 4-3). In the \( x \)-direction there is advection and possibly diffusion.

\[
\nabla \cdot N_x = -D \nabla^2 c + \bar{u} \nabla c \quad (4.18)
\]

The leading term of diffusion, \( D_{NaCl}/L_c^2 \) was compared to advection, \( \bar{u}/L_c \). For channel lengths on the order of 0.1 m and diffusivity on the order of \( 10^{-9} \) m, the diffusion term has a magnitude of \( \mathcal{O}(10^{-7}) \). For flow velocities greater than \( 10^{-8} \) m\(^2\)/s the advection transport rate will be much greater than the diffusion. Therefore diffusion in the \( x \)-direction is negligible.

In the spacer, the fluxes in the \( y \)-direction are driven by diffusion (no flow velocity for steady state laminar flow, from continuity). Because the cell operates with advection dominance in the \( x \)-direction, we can approximate that the concentration gradients in the bulk are limited to the mass flux boundary layer between the spacer

Figure 4-2: Half-cell model schematic
and the electrode \[149\].

\[ N_y \sim D(c - c_e)/\delta(x) \]  \hspace{1cm} (4.19)

The mass transfer boundary layer, \(\delta(x)\) is derived previously for flux into porous media \[149\]:

\[ \delta(x) = 1.475 \left( \frac{h D x}{u_{\text{max}}} \right)^{\frac{1}{2}} \]  \hspace{1cm} (4.20)

Therefore we modeled the space in the channel as a 1D finite element system, with a diffusive flux in the \(y\)-direction matched with the flux into the electrode, and advective flux in the \(x\)-direction (Figure 4-3a).

In the electrode, we considered whether the \(x\)-direction flow \(\Phi\) would flow through both the electrode and spacer, or just the spacer. For low Reynolds flow, we assumed the pressure drop follows Darcy’s law. Then the permeability, \(\kappa\) will be proportional to the volume to area ratio of the porous media, \(\kappa \approx d_e^2 \sim (40 \text{ nm})^2 = 1.6 \times 10^{-15} \text{ m}^2\) \[149\], which is very impermeable compared to the open space in the gap. Therefore, we assumed advection only occurs through the spacer and not in the electrode.

In the electrode, we compared concentration gradients to determine the relative magnitudes of diffusion in \(x\) and \(y\). The concentration gradients in the \(x\) and \(y\):

\[ \frac{\partial^2 c_e}{\partial x^2} \sim \Delta c_e/L_e^2 \]  \hspace{1cm} \text{and} \hspace{1cm}

\[ \frac{\partial^2 c_e}{\partial y^2} \sim \Delta c_e/L_e^2. \]

Since \(L_e \ll L_c\), we assumed diffusion in the \(y\)-direction is much greater than in the \(x\)-direction so we modeled diffusion only in \(y\) for simplicity (Figure 4-3b). However, future models could relax this assumption.

Finally, rather than modeling the electromigration terms, we assumed that electrode charging is fast compared to the diffusion, and take an empirical approximation for the electrode charging fluxes. This will be discussed in greater detail in section 4.2.1. Therefore, in the electrode we ultimately modeled 1D diffusion in the \(y\)-direction.

Taking the aforementioned assumptions into consideration, we derived the control volume conservation of mass in the spacer channel (schematic represented in Figure 4-3).

\[ L_{sp} b \frac{\partial c}{\partial t} = \Phi \frac{\partial c}{\partial x} - \frac{D}{\delta(x)}(c - c_e)b \]  \hspace{1cm} (4.21)
In the electrode, the conservation of mass is given by the 1D diffusion in y.

$$\frac{\partial c_e}{\partial t} = -D_e \frac{\partial^2 c}{\partial y^2} \quad (4.22)$$

Finally, the boundary conditions for the cell are constant inlet concentration $c(x = 0, t) = c_\infty$, no flux out the backside of the electrode $-\partial c_e/\partial y \mid_{y=L_e} = 0$, and matching fluxes from the spacer to the electrode, $D \partial c/\partial y \mid_{y=0} = D_e \partial c_e/\partial y \mid_{y=0}$.

### 4.2.1 Electrode Charging and Initial Conditions

The cell begins initially saturated with the bulk concentration, $c(x, t = 0) = c_\infty$. In the electrode, double layer charging is assumed to be much faster than diffusion from the spacer into the electrode. Thus, we initialized the model $t = 0$ after the double layer is charged, modeled as a pulse. Therefore, the electrode concentration at the start of the simulation is, $c_e(x, y, t = 0) = c_\infty - c_{rem}$, where $c_{rem}$ is the concentration of charge adsorbed by the electrode when it is fully charged. In an experiment, this is determined by allowing the CDI cell to achieve maximum salt adsorption through long cycling times and slow flow rates. It is possible to estimate $c_{rem}$ as a function of applied voltage, by approximately converting it from a given electrode’s capacitance.

For example, a 10 F/cm$^3$ cell operating at 1.2V would remove $c_{rem} = 10 [\text{F/cm}^3] \times 1.2 \text{V} \times \frac{1 [\text{mol}]}{96,485 [\text{C}]} \times \frac{10^6 [\text{cm}^3]}{[\text{mol}^3]} = 124 [\text{mM}]$. At the time of discharge, the salt removed is
released back into the electrode: \( c_e(x, y, t = t_{cycle}/2) = c_e(x, y, t_{cycle}/2 - dt) + c_{rem} \).

This approach provides a basic mechanism for simulating charge/discharge in the cell. We will revisit this approach later in the chapter and discuss refinements further.

### 4.2.2 Non-Dimensionalization

We non-dimensionalized the equations in order to determine the important contributors to solving unique effluent salt concentration profile solutions. Typically, \( c_{out} \) is normalized by \( c_\infty \). However, because the initial charging of the electrode is dependent on \( c_{rem} \), we used a normalization of concentration depletion with respect to the maximum amount of salt that can be removed.

\[
c^* = \frac{c - c_\infty}{c_{rem}}
\]  

(4.23)

The time was scaled by the diffusion time constant.

\[
\tau^* = \frac{t}{\tau_d} = \frac{tD_e}{L_e^2}
\]

(4.24)

The spatial coordinates were non-dimensionalized by their characteristic length scale.

\[
x^* = \frac{x}{L_e}, \quad y^* = \frac{y}{L_e}, \quad \delta^* = \frac{\delta}{L_e}
\]

(4.25)

Then, returning to the governing equations 4.21 and 4.22, the non-dimensional conservation equations are:

\[
\frac{\partial c^*}{\partial t^*} = \frac{\Phi L_e^2}{bL_{sp}L_e D_e} \left( - \frac{\partial c^*}{\partial x^*} \right) - \frac{L_e}{L_{sp}} \left( \frac{c^* - c^*_e}{\delta^*} \right) - \frac{\partial c^*_e}{\partial y^*^2}
\]

(4.26)

\[
\frac{\partial c^*_e}{\partial t^*} = \frac{\partial^2 c^*_e}{\partial y^*^2}
\]

(4.27)

These governing equations imply that all solutions to the system of equations are dependent on an advection-diffusion Péclet number comparing the advection in the
Figure 4-4: Schematic of the advection-diffusion Péclet number and varying $L_{rat}$

channel to the diffusion in the electrode, $\tilde{P}e = \tau_{c,x}/\tau_{d,y}$ and the electrode thickness ratios, $L_{rat}$, comparing the electrode thickness to the spacer thickness. In Figure 4-4 these two parameters are illustrated.

Finally, the initial and boundary conditions in non-dimensional form are given below. The salt concentration in the channel initially is zero.

$$c^*(x^*, t^* = 0) = 0 \quad (4.28)$$

The electrode concentration initially at charging is -1.

$$c_e^*(x^*, y^*, t^*) = -1 \quad (c_e^* = c_e^* + 1 \text{ discharge}) \quad (4.29)$$

Finally, the boundary conditions are (1) constant inlet concentration $c^*(x^* = 0, t^*) = 0$, (2) no flux at the backside $\frac{\partial c_e^*}{\partial y^*} |_{y^*=1} = 0$, and (3) flux matching between electrode and spacer, $\frac{\partial c_e^*}{\partial y^*} |_{y^*=0} = \frac{\epsilon}{\tau} \frac{\partial c_e^*}{\partial y^*} |_{y^*=0}$.

The mass transfer boundary layer thickness grows until it intercepts the channel length. This is normalized below.

$$\delta(x) = \begin{cases} 1.475 \left( \frac{\tau_{d,y}}{Pee \ L_{rat}} \right)^{\frac{3}{2}} & \delta^* < \frac{1}{L_{rat}} \\ \frac{1}{L_{rat}} & \delta^* \geq \frac{1}{L_{rat}} \end{cases}$$

Finally, we non-dimensionalize key characteristics of CDI, equations 3.8 and 3.9.
and the salt rejection definition, equation [4.1]. The salt adsorption is:

$$S_{ads}^* = -\frac{\tilde{P}e}{L_{rat}} \int c^* dt^*$$  (4.30)

The salt adsorption rate is:

$$S_{rate}^* = \frac{S_{ads}^*}{\Delta t^*}$$  (4.31)

Finally the salt rejection, $SR = 1 - \frac{c_{out}}{c_{\infty}}$ can be written non-dimensionally as:

$$SR^* = \frac{c_{\infty}}{c_{rem}} SR$$  (4.32)

This derived system of equations can now be used to simulate CDI cells of varying parameters over time.

4.3 Model and Data Acquisition Set Up

In this section, we outline how the model was implemented and how flow-cell CDI experiments were conducted to validate the model.

4.3.1 Computational Implementation

We used forward Euler in time, first-order backward difference for concentration gradients and second-order difference equations for diffusion gradients. Simulations presented in this section were for a discretized grid of $N_x = 4$ elements and $N_y = 4$ elements, creating a 16 element grid. In order to select a time-step that maintained computational stability we compared the leading terms in the governing equations 4.26 and 4.27 when discretized.

$$\frac{c_{i}^{t+1} - c_{i}^{t}}{\Delta t} = \tilde{P}e - \frac{-(c_{i}^{t} - c_{i-1}^{t})}{\Delta x} - L_{rat} \frac{c_{i}^{t} - c_{e,i,j=0}^{t}}{\delta^*(x^*)}$$  (4.33)

$$\frac{c_{e,j}^{t+1} - c_{e,j}^{t}}{\Delta t} = \frac{c_{e,j-1}^{t} - 2c_{e,j}^{t} + c_{e,j+1}^{t}}{\Delta t^2}$$  (4.34)
Figure 4-5: Example simulation results. a) Effluent concentration profile simulated during charge-discharge. b) Simulated salt rejection during charging.

From the above equations we can determine two criteria for the size of the time step $\Delta t$.

$$
\Delta t < \frac{\delta^*(x^*) \Delta x^*}{Pe \delta^*(x^*) + L_{\text{rat}} \Delta x^*}
$$

(4.35)

$$
\Delta t < \frac{\Delta y^*}{2}
$$

(4.36)

The simulations run stably as long as $\Delta t$ is less than both inequalities. Example simulation code is provided in Appendix C.

4.3.2 Experimental Set Up

Experiments were conducted similarly to what was outlined in Chapter 3. In these experiments, the gap of the flow cell was created using plastic shims, taped in place and epoxied on the outside for sealing. This was to ensure that the spacer thickness was as precise as possible for macroscale flow cells. We used 2 x 8 cm VA-CNT forests of varying heights, $L_e$, in order to design cells with varying $L_{\text{rat}}$. The exact experiment parameters for each flow cell are given in Appendix D.
4.3.3 Experimental Uncertainty Analysis

Uncertainty analysis of the experimental data was conducted using propagation of error based on the governing equations 4.30, 4.46. Uncertainty of geometry and variation in the CNT forest height were determined by taking multiple measurements of cells and samples and calculating the variance. Salt adsorption uncertainty was calculated by looking at variations between cycles, and also by examining the variation in the time-integration depending on whether the initial or final concentration value was used as the limit (due to fluctuations in conductivity measurement from temperature sensitivity and the presence of adsorption/desorption inversion peaks).

The uncertainty, $\sigma$, in the concentration of salt removed was calculated from propagation of error.

$$
(\sigma_{rem})^2 = \left(\frac{1}{bL_e L_c}\right)^2 \sigma_{out}^2 + \left(\frac{-S_{out}}{bL_e L_c}\right)^2 \sigma b^2 + \left(\frac{-S_{out}}{bL_e L_c^2 L_e}\right)^2 \sigma L_e^2 + \left(\frac{-S_{out}}{bL_e L_e^2}\right)^2 \sigma L_e^2
$$

(4.37)

Then the uncertainty of the non-dimensional salt concentration, $\sigma c^*$ defined in equation 4.23 is simply:

$$
(\sigma c^*)^2 = \left(\frac{c_{\infty} - c}{c_{rem}^2}\right)^2 \sigma_{rem}^2.
$$

(4.38)

The uncertainty of the non-dimensional time constant, $\sigma t^*$ is based on uncertainties in calculating the electrode thickness (the diffusivity and time measurement uncertainty are relatively small).

$$
(\sigma t^*)^2 = \left(\frac{-2D_e t}{L_e^3}\right)^2 \sigma L_e^2
$$

(4.39)

The error of the non-dimensional salt rejection based on equation 4.32 can be calculated from the above uncertainties.

$$
(\sigma S R^*)^2 = \left(\frac{-S R c_{\infty}}{c_{rem}^2}\right)^2 \sigma_{rem}^2
$$

(4.40)

Finally the uncertainty of $L_{rat}$ and $Pe$ number can be calculated from their definitions (Equation 4.26).
Figure 4-6: Model analysis of salt rejection and salt rejection rate for varying $\tilde{P}_e$ and $L_{rat}$. $c_{rem} = \pm 1$ at $t = 0$.

\begin{align*}
(\sigma_{L_{rat}})^2 &= \left(\frac{1}{L_{sp}}\right)^2 \sigma_{L_e^2} + \left(\frac{-L_e}{L_{sp}^2} \right)^2 \sigma_{L_{sp}^2} 
\end{align*}

\begin{align*}
(\sigma_{\tilde{P}_e})^2 &= \left(\frac{L_e^2}{L_{sp}L_{cb}D_e} \right)^2 \sigma_{\Phi^2} + \left(\frac{2\Phi L_e}{L_{sp}L_{cb}D_e} \right)^2 \sigma_{\epsilon_e}^2 + \left(\frac{-\Phi L_e^2}{L_{sp}^2 L_{cb}D_e} \right)^2 \sigma_{L_{sp}^2} + \\
&\quad + \left(\frac{-\Phi L_e^2}{L_{sp}L_{cb}D_e} \right)^2 \sigma_{\epsilon_c}^2 + \left(\frac{-\Phi L_e^2}{L_{sp}L_{cb}^2 D_e} \right)^2 \sigma_{b^2}^2
\end{align*}

4.4 Model Validation and Analysis

Model validation was conducted by comparing steady-state simulations (i.e. fully charging and discharging the electrode) to experimental results, using the maximum salt rejection analysis as outlined in Figure 4-1. The simulation was run, cycling charge and discharge, and integrating to find the salt rejection over time, as shown in Figure 4-5.

For varying $\tilde{P}_e$ and $L_{rat}$, the maximum salt rejection, $SR^*$ was calculated. Comparing simulation results in Figure 4-6 for varying $\tilde{P}_e$ and $L_{rat}$, we found that the maximum salt rejection increases with the increase electrode-spacer length scale ratio and that at low $\tilde{P}_e$ and high $L_{rat}$ the salt rejection converges to 100%. There is also a frequency at which the $SR^*$ begins to drop off for a given $\tilde{P}_e$, though increasing
Figure 4-7: Optimal salt rejection calculated from simulation (solid line) compared to data.

$L_{\text{rat}}$ pushes the drop-off frequency to higher $\tilde{Pe}$ numbers. The salt adsorption rate generally increases with $\tilde{Pe}$ number as expected. However, there seems to be a trend that at $\tilde{Pe} < 1$ lower $L_{\text{rat}}$ have higher desalination rates but at higher $\tilde{Pe}$ this trend is reversed. This is likely due to the limits of advection versus diffusion in the system.

We built and studied four experimental flow cells from $L_s p$ 0.6 to 7.8. The results in Figure 4-7 show that the simulation overpredicts $SR_{\text{opt}}^*$ for all cells of varying $L_{\text{rat}}$. This is due to the simulation electrode charging modeled as an instantaneous pulse. In reality, the charging of the double layer will be dependent on the moles of salt present in the electrode, supplied to the electrode, and diffusion through the electrode. In order to account for this, we reconsidered using a pulse for the salt removal in the
4.4.1 Reconsidering Charging Kinetic Modeling

The charging profile was slowed down from a pulse, to a single time-constant, $\tau$, exponential function, as shown in Figure 4-8.

In order to determine an appropriate $\tau$, we considered when the electrode charging will either be limited by advection, diffusion, or the linear transmission line charging time scale. As $\tilde{Pe} = \frac{\tau d}{\tau_c}$, it can be shown how the $\tilde{Pe}$ number defines the appropriate $\tau$ for the system.

$$\tau^* = \begin{cases} 
\frac{1}{\tilde{Pe}}, & \tilde{Pe} < 1 \quad \text{advection - limited} \\
1, & \tilde{Pe} > 1 \quad \text{diffusion - limited} \\
\frac{\lambda d}{h_p}, & \tilde{Pe} \gg 1 \quad \text{supercapacitor - regime}
\end{cases} \quad (4.43)$$

This approach agrees with Biesheuvel and Bazant [134] who showed $\tau = \frac{\lambda d}{h_p}$ for a linear transmission line model, and that $\tau = \tau_d$ for the nonlinear transmission line model, which agrees with our analysis when $\tilde{Pe} > 1$. In addition, we show that for low $\tilde{Pe}$, when the cell is advection-limited the time constant for charging will be closer to $\tau = \tau_c$. 

Figure 4-8: Charging profile in the simulation. Pulse (orange) vs Exponential (blue).
Using this approach we revised equation 4.27

\[ \frac{\partial c_e^*}{\partial t^*} = \frac{\partial^2 c_e^*}{\partial y^*^2} - c_{rem}(t^*) \]  

(4.44)

where \( c_{rem}(t^*) \) is defined by an exponential function that integrates to \( \pm 1 \) from \( 0 < t < 5\tau \).

\[
  c_{rem}(t^*) = \begin{cases} 
    A_o(-1 + \exp(-t/\tau)), & \text{charging} \\
    A_o(1 - \exp(-t/\tau)), & \text{discharging} 
  \end{cases} 
\]

(4.45)

The constant \( A_o = \frac{1}{4\tau + \tau \exp^{-5}} \) satisfies the integral. Accounting for the varying time scales of the system in our simulation leads to very good agreement between simulation and experimental results, as shown in Figure 4-9. The magnitude of the peaks in the effluent and general characteristics match between experiment and simulation. However, the simulation is broader and less sharp, compared to experiment because the early-time non-linear dynamics of desalination are not captured. For this reason, the simulation salt rejection under-predicts the experiment. However, at long time scales the salt rejection between experiment and simulation show good agreement. This suggests that while the exact value of the effluent concentration and salt rejection will be under-predicted by the model, the time scales and overall magnitudes are similar, such that trends can be conservatively studied with our model.
Figure 4-10: Model analysis of salt rejection for varying $\tilde{Pe}$ and $L_{rat}$. Charging is simulated with an exponential function of varying $\tau$ dependent on $Pe$ number.

The simulation updated with Equation 4.44 was compared to experimental results. The salt rejection (Figure 4-10) follows a similar trend as the pulse charging simulation, but the magnitudes are much lower when accounting for advection and diffusion limitations for charging. The simulation generally under-predicts the experimental values, though at high aspect ratios the model over-predicts the experiment. This discrepancy is likely due to the experimental measurement. Due to the long time scales for charging the electrode it is possible that salt does not diffuse into the full volume of the electrode. In addition, it is difficult to measure small changes in the concentration (< 2%) with a conductivity meter and we may not be able to resolve to the total salt adsorption of the electrode in experiment. In general, the simulation and experimental results, have similar trends, suggesting that an appropriate empirical model for the charging and discharging of the electrode can be used to simplify analysis and focus on device design optimization.
4.5 Maximizing Salt Rejection in a CDI Device

In the previous section, the simulation showed that the salt rejection has a proportional dependency on $L_{rat}$ and inverse relationship with $\tilde{P}e$. This can also be deduced analytically from the governing equations. Combining Equations 4.32 and 4.30 yields an equation for salt rejection in terms of the key cell parameters.

$$SR^* = \frac{L_{rat} S^*_{ads}(t)}{\tilde{P}e \Delta t^*}$$  (4.46)

From Equation 4.46, several important relationships for maximizing salt rejection can be determined. By increasing $L_{rat}$ or decreasing $\tilde{P}e$, the salt rejection will also increase. Previously Porada et al showed that a CDI cell had improved performance with increasing electrode thickness [142], while Liu et al. showed reducing spacer thickness can do the same [147]. These experimental observations are in agreement with the model’s $L_{rat}$ analysis. The salt adsorption and cycle time are coupled. If the time is sufficiently long, $S^*_{ads} = 1$ but if $\Delta t^*$ is too long than $SR$ will go to zero. However, if the cycling is very fast but $S^*_{ads} \to 0$, then $SR$ will also go to zero. This suggests, tuning the frequency of the duty cycle can yield an optimal salt rejection.

This last point, the role of cycling frequency on effluent concentration profile, can be illustrated by looking at simulation results for a fixed $\tilde{P}e$ and $L_{rat}$ cell, shown in Figure 4-11. As expected, at high frequencies there is no perturbation in the effluent concentration, but as the cycle time is increased the peak concentration increases until it maximizes for complete desalination from the bulk.

In the previous section, Figure 4-10, showed that increasing the $\tilde{P}e$ led to reduced optimal $SR^*$. In addition, we increased $L_{rat}$ led to increased optimal $SR^*$, agreeing with the above analysis. In this section, we will simulate the space of varying $\tilde{P}e$, $L_{rat}$, and $f^*$ and its effect on $SR^*$.  

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(a) $f^* = 10$

(b) $f^* = 1$

(c) $f^* = 0.1$

(d) $f^* = 0.01$

(e) $f^* = 0.001$

(f) $f^* = 0.0001$

Figure 4-11: Effluent salt concentration profiles for varying charge-discharge duty cycles. All simulations run for $\tilde{Pe} = 0.3$ and $L_{rat} = 5$.

4.5.1 Maximum Salt Rejection for any Device

Simulations were conducted for varying $L_{rat}$ between 0.5 to 10, varying the $\tilde{Pe}$ number and the cycling frequency $f^*$ to find the combination yielding the highest salt rejection. The simulations were run until the cycling values stabilized and each cycle yielded the same result. $SR^*$ for the charging phase was calculated. The results of the analysis are plotted in Figure 4-12.

As $L_{rat}$ increases the salt rejection magnitude increases for a cell very dramatically. This suggests that having an electrode much thicker than the spacer channel is important for desalination. In addition $\tilde{Pe}$ numbers <1 yield much higher salt rejection. Therefore, if one needs high flow rates they will need to reduce the thickness of the electrode and increase the channel lengths, and widths of the system.

In addition, there are two bounds for the salt rejection, which can be understood by looking at the salt adsorption curves. At low frequencies when the cell is fully charged, salt rejection begins to drop off due to the run time following desalination of the cell. At high frequencies, salt rejection begins to drop off when the cell is no longer removing enough salt from the bulk. In addition, while the salt adsorption
Figure 4-12: Salt rejection (left column) and salt adsorption (right column) at varying cycling frequencies and $\tilde{P}e$ numbers.
Figure 4-13: $\tilde{Pe} = 0.2$ salt rejection and salt adsorption. Colored lines are varying $L_{rat}$ from 0.5 to 10.

profiles are not exactly the same for varying $L_{rat}$, they are similar enough that the charge profile can be approximated from one solution of the differential equations.

Examining a slice of these contour plots, varying frequency but fixing $\tilde{Pe}$, shows the dependency of $SR^*$ and $L_{rat}$. (Figures 4-13-4-15). At $\tilde{Pe} < 1$, the maximum frequency is higher for lower $L_{rat}$ and the $S_{ads}^*$ is greater. The $S_{ads}^*$ is greater in this situation because low aspect ratio devices are able to respond to the charging/discharging faster in the transport limited situation. At $\tilde{Pe} \gg 1$ the peak salt rejection occurs at similar frequencies and the salt adsorption profiles are identical because the system is diffusion-limited, not advection-limited.

4.5.2 Experimental Results

CDI experiments were conducted at $\tilde{Pe} = 10^{-0.5}$ to operate close to the maximum predicted salt rejection. Flow cell experiments were run between mHz to Hz frequencies (non-dimensionalized by the diffusion time constant). Two flow cells were investigated with a $L_{rat}$ of 0.8 and 6.3 in 1 mM NaCl. Experimental results show similar trends to the model prediction as shown in Figure 4-16. For the $L_{rat} = 0.8$ electrode, the
Figure 4-14: $\tilde{P}e = 1$ salt rejection and salt adsorption. Colored lines are varying $L_{rat}$ from 0.5 to 10.

Figure 4-15: $\tilde{P}e = 29$ salt rejection and salt adsorption. Colored lines are varying $L_{rat}$ from 0.5 to 10.
Figure 4-16: $\tilde{Pe} = 10^{-0.5}$ a) salt rejection and b) salt adsorption. Colored lines are simulation and symbols are experimental data.
Experimental results had slightly higher salt rejection ratios, as expected, due to the faster dynamics of the electrode not captured in a single exponential system. Optimal salt rejection was achieved around $f^* = 0.05$ while the electrode was fully charged at $f^* = .03$; thus, slightly faster cycling times for maximum salt adsorption is recommended. In the $L_{rat} = 6.3$ system, the maximum salt rejection frequency was less dramatic than the $L_{rat} = 0.8$ system, and occurs at a frequency of $f^* = 0.02$. Similar to the model prediction, the thicker aspect ratio system had a maximum frequency to the left of the thin system. In the $L_{rat} = 0.8$ system, the model slightly over predicted the salt rejection. Similar to the previous observations in the steady-state analysis, this may be due to the slow charging of the electrode in the experiments, which may lead to under-utilization of the full electrode volume for desalination or inaccuracy in measuring very small changes in effluent conductivity.

4.6 Conclusions

In this chapter, we developed a model that can provide insight into how to design a CDI cell for maximum salt rejection. We developed an advection-diffusion model that used an empirical equation for simulating the charging and discharging of the electrodes. This allowed us to focus on the role of device geometry and specifications on desalination performance. This is the first approach to study and experimentally validate the limitations of flow parameters and duty cycling on flow-between CDI systems in continuous operation.

We determined that operating at $\bar{Pe} < 1$ with high aspect ratio electrodes is the key to achieving the maximum desalination. In addition, the duty cycle frequency where this maximum occurs is about 1.6 times shorter than complete charging of the electrode. However, at high $\bar{Pe}$ numbers the maximum salt rejection cycling time is the same as charging time.

Finally, in order to keep an overall system time that is short, reducing the thickness of the electrodes, $L_e$ so that the diffusion and advection time constants are reduced will help keep fast cycling times.
For the first time, we have provided a framework for studying device design parameters for a CDI cell. We have varied flow parameters, electrode thicknesses, gap thicknesses, and cycling frequency in order to characterize these variables’ role in salt rejection. This can be used immediately by researchers to determine how to size their system for laboratory experiments and beyond.

In the future, by coupling this model with an electric double layer model or an approximated non-linear transmission line model, we can also simulate the energy consumption in order to determine the salt-rejection vs energy consumption curves to compare CDI to existing desalination systems such as RO or ED.
Chapter 5

Conclusions

5.1 Thesis Summary

The goal of this thesis was to design a framework to better understand how to design a CDI device for maximum desalination performance. We did this by developing vertically-aligned carbon nanotube electrodes as a platform for studying the coupling of electrodes and devices in CDI.

In Chapter 2, we studied VA-CNT electrodes in a traditional supercapacitor characterization set-up. We found that in 1 M NaCl, VA-CNTs produced capacitances between 22-35 F/g. In addition, by developing a modified transmission line model we were able to characterize the surface area to volume ratio, which can be used to estimate charging time constants of supercapacitor electrodes. In addition, by considering the coordinate number of VA-CNT packing, we could also estimate the inter-CNT spacing for sparse and dense forests.

In Chapter 3, we integrated VA-CNT electrodes into a flow-between CDI device, introducing a novel material to the CDI community. By tuning experimental conditions and the electrode properties we were able to demonstrate upto 8 mg/g salt adsorption and rates upto 0.6 mg/g-min. However, we also determined that the electrode degradation at voltages greater than 1.5V were significant and lead to electrode failure over a few days. Annealing CNTs at high temperatures and scaffolding with other carbon materials could yield more stable and higher performance devices.
In Chapter 4, we developed a mass transport model that gave new insight into the key parameters for sizing flow-between CDI devices for research and industrial set ups. We showed that by using a holistic exponential function to approximate electrode charging, we could approximate the system desalination dynamics. By increasing the electrode thickness and reducing the spacer thickness higher salt rejection is possible. In addition, reducing the advection-diffusion $Pe$ number through decreased flow rates, or increased cell volume, can increase salt rejection as well. We also showed that at low $Pe$ numbers, a duty cycle that is $\sim 1.6$ times faster than the full electrode charging time can maximize salt rejection, while also reducing cycle time. For the first time, we have demonstrated key relationships between electrode thickness, spacer thickness, flow parameters, and duty cycling on cell desalination performance.

5.2 Thesis Contributions

- We designed an electrode configuration using delaminated vertically-aligned carbon nanotubes (VA-CNTs) to serve as a platform for studying fundamental electrode properties and simple geometries for manipulating desalination performance in a flow-between capacitive deionization cell.

- We developed and applied a novel method, using a modified transmission line model, to calculate the distribution inter-CNT spacings in VA-CNT forests of varying densities by projecting the surface area to volume ratio accurately. This *in situ* method could provide porous electrode analysis as an alternative to BET surface area and imaging techniques.

- We demonstrated the first comprehensive use of VA-CNT electrodes in CDI devices, and showed that bare electrodes can adsorb up to 8 mg salt /g electrode material. In addition, we demonstrated that by varying the carpet height and density we can directly change the desalination rate proportional to the electrode diffusion time constant.

- We created an advection-diffusion model that is electrode agnostic, using a gen-
eralized approach that can predict performance for any electrode material. By deriving the non-dimensional salt rejection as $SR^* = \frac{L_{ads} S_{ads}}{Pc \Delta t^*}$, we demonstrated the importance of the electrode thickness to spacer ratio, the Péclet number, and cycling on driving salt rejection for the system. This analysis was validated with CDI experiments utilizing VA-CNT electrodes.

5.3 Future Work

There are many opportunities going forward with the framework presented here. In Chapter 3, we studied the adsorption properties of bare VA-CNTs. Developing hierarchical CNT structures may create the salt adsorption capacity needed to compete with other hybrid monolithic materials. In Chapter 4, we developed a desalination model that was validated against as-grown, macroporous VA-CNT forests. Extending the validation of the model framework using other common electrode materials would be a suitable way to determine if both microporous and macroporous materials can be utilized by this holistic approach. Finally, extending this analysis to other CDI configurations such as flow-through could help determine trade-offs and opportunities for CDI in industrial applications.

5.3.1 Hierarchical CNT Structures

There has been significant materials development on creating hierarchical carbon structures, with a lot of work focused on integrating loose carbon nanotubes with other carbons or coatings. Previous work has shown that a combination of carbon nanotubes with activated carbon [150] or ordered mesoporous carbons [36 47 151] can increase charge efficiency in CDI due to increased electrode conductivity and capacitance. However, these materials still had <1 mg/g salt adsorption capacity. Another approach has been using CNTs with graphene oxide [152] or graphene [63 153]. Graphene increases electrode conductivity significantly, and improves overall capacitance. Wimalasiri and Zou [63] demonstrated an adsorption capacity of 26.4 mg/g, much higher than previous aerogel capacity. In addition Sui et al. demonstrated
Figure 5-1: Proposed approach for further development of VA-CNT electrodes for CDI. Increasing the surface area through polymer coatings (green) or tuning surface chemistry could increase the adsorption capacity of CNTs while maintaining the porous diffusivity and charging rate.

that the addition of graphene, chemical functionalization, and hierarchical porous structures in aerogel could lead to very high desalination (potentially up to 633 mg/g salt adsorption in 0.5 M NaCl). However this analysis was based on capacitor measurements and fitting a Langmuir isotherm which could over-predict the electrode adsorption capacity in CDI [64]. Nevertheless, the work done with loose CNTs suggests that developing a monolithic electrode combining VA-CNTs with another highly conductive carbon such as graphene could enable a high adsorption CDI device.

In addition to creating carbon-carbon structures, tuning the pore sizes of the electrode, as well as the surface chemistry can increase charge efficiency and overall desalination [40]. There have been two main approaches to this: either including metal oxides in carbon matrices [62], or introducing polymer coatings on top of the carbon matrix. One approach has been to coat carbon with chitosan, which has been shown to increase copper ion removal in CDI [154, 155], up-to 85% more than uncoated carbon. Polyaniline (PANI) has also been used in CNT systems [46]. PANI increases surface areas, and due to $\pi - \pi$ bonding with CNTs it has minimal resistance between the CNTs and the polymer matrix. PANI has been shown to improve efficiency in CDI, due to the increased surface area and improved surface chemistry. In addition, coating the cathode with an ion exchange membrane polymer can improve charge efficiency due to the prevention of co-ion adsorption [113].
In supercapacitor literature, extensive research on coatings has also been conducted \([78, 156]\). A comparison of PANI vs PEDOT coatings on carbon has suggested similar performance between the two polymers, though PEDOT has a higher voltage stability window for capacitance (-0.7 to 0.7 V vs Ag/AgCl). We have conducted preliminary studies using PEDOT on VA-CNT forests, but have found that the ionic resistance is too high to gain adsorption capacity. Tuning the coatings with the matrix, will be very important to maintaining electrode charging dynamics while increasing desalination.

In summary, VA-CNTs could be promising for CDI through an increase in surface area and a tuning of electrode chemistry (Figure 5-1). With polymer coatings and incorporation of other high conductivity carbon materials, VA-CNTs could provide fast, effective desalination.

### 5.3.2 Extending the Advection-Diffusion Model

From the model developed in Chapter 4, there are two main paths for extending the model. The first is to focus on the electrode kinetics, by either incorporating electric double layer models into the system or studying the use of this model on other carbon materials. The latter is important for considering how to empirically capture mass transport in materials that have both macro and micropores. By looking at materials such as activated carbon, carbon aerogel, or mesoporous carbons, using a similar framework outlined in Chapter 4 for VA-CNTs, we can validate if this approach holds for many types of materials.

The second opportunity is to use the developed model to compare water recovery in CDI and other desalination systems. At present, Jande and Kim’s model \([145]\) has been used to consider the design of hybrid RO-CDI systems \([157, 158]\). However, this model and our model are limited in quantifying the energy consumption of the CDI component. Both solutions can determine pumping power, but only by assuming a CDI charge efficiency are we able to convert desalination performance to the current consumption. From experiment, we know that charge efficiency is voltage dependent, but also dependent on feed concentration, resistances in the system, etc. In order to
strengthen our advection-diffusion model, re-incorporating a transmission line model may allow us to get more realistic energy recovery for comparing performance of CDI, RO, and ED more directly. Ultimately, the model developed in this thesis can provide a stepping stone to compare CDI with existing desalination technologies.
Appendix A

CDI Experimental Design

Considerations

Through the process of designing and running flow-between CDI experiments, we have found a few things to consider that are important for high quality measurements. We alluded to some of these things in Chapter 3, but here we will focus on system sizing and ion selective probe measurements.

A.1 CDI Cell Design

When we began this project, we initially designed cells based on volumetric salt adsorption capacity, with little consideration for the spacer thickness and system volume. We began by running experiments with electrodes that were only 100-250 microns thick, with spacers that were 1 mm ($L_{rat} = 0.1 - 0.25$). We found that the effluent concentration in these cells changed imperceptibly. Often, the conductivity probe readings fluctuated more due to temperature changes in the room than due to desalination. We then re-sized the cell for electrodes that were 1 mm thick with spacers that were 350 microns ($L_{rat} = 6.3$). This allowed for better, measurable signals (prototype 1). Our analysis in Chapter 4 backs up this experimental finding: increasing the electrode to spacer thickness ratio yields larger fluctuations in the effluent concentration. Thus, the model in Chapter 4 can be used for both research
cell design and industrial desalination applications.

In addition, we observed that ensuring the cell is fully wetted is crucial to experiments measuring the salt adsorption of the electrode material. Initial designs of the flow cell placed the ports on one half of the electrode, which did not guarantee that bubbles would exit during the initial purging. Therefore, we saw low performance and high variability between experiments. The prototypes presented in the main text used inlet and outlet ports on opposite electrodes, with the outlet on top, allowing for bubbles to escape.

Finally, we found that the initial wetting of the electrode is best at moderate flow rates (1-2 mL/min) to ensure the cell is fully evacuated. We found that if we began operating the cell only at low flow rates (0.1-1 mL/min), we observed low gravimetric salt adsorption. Thus, starting at moderate flow, and then either reducing or increasing for the experiment ensured greater repeatability of the cell.

A.2 Ion-Selective Probe Measurements

In our experiments, we measured effluent conductivity and converted it to NaCl. However, conductivity, $\kappa$ is a bulk measurement and is the sum of all ionic conductances including proton and hydroxide groups.

$$\kappa = \Sigma \kappa_{ions} = \kappa_{Na^+} + \kappa_{Cl^-} + \kappa_{H^+} + \kappa_{OH^-}$$  \hspace{1cm} (A.1)

In Chapter 3, we mentioned several possible Faradaic reactions that could occur at the applied voltages used in our CDI set up. By only measuring inlet and outlet conductivity we can not easily distinguish changes in surface chemistry or onset of electrolysis in the system. Previous work [44, 127] has incorporated pH measurements into their system, showing that while the conductance contribution is small compared to NaCl, it can give insight into changes in the electrode. If we reconsider the Nernst-Einstein conductivity from equation 3.2, we can include protons and hydroxide groups in the summation, $\kappa = \Sigma \Lambda_a^{\gamma_i} c_i$. From Kohlrausch, we see that
\( \Lambda_m^0 \) for \( H^+ = 349 \) while \( Na^+ = 50 \); therefore if the \( \text{pH} \) is >4, it will have negligible contributions on converting conductivity directly to NaCl concentrations.

However, measuring each individual ion (Na\(^+\), Cl\(^-\), H\(^+\)) would give greater insight into any reactions occurring in the system. In pursuit of this, we developed a setup with \( \text{pH} \) probes, sodium probes, and chloride probes at the inlet and outlet. The \( \text{pH} \) probes and sodium probes were purchased commercially (Cole Parmer, Oakton refillable \( \text{pH} \) probe GH-35805-04; Microelectrodes, Inc., MI-409, Flow-Through Na probe). The chloride probe was a lab-made sensor comprised of an electroplated Ag wire in KCl to form an Ag/AgCl coated wire that was plugged into a barbed-tee for direct connection to solution. The premise for all measurements is the same: by measuring a difference in voltage between the probe and an Ag/AgCl reference of fixed concentration, we can calculate the concentration of a specific ion using the Nernst equation. The \( \text{pH} \) concentration-voltage relationship can be determined from the reaction \( 2 \text{H}^+ + 2e^- \leftrightarrow \text{H}_2(\text{g}) \).

\[
E_{PH} = E_o + \frac{2.303RT}{F} \log([H^+]) \quad (A.2)
\]

Similarly, the sodium concentration-voltage relationship can be determined from the reaction \( \text{Na}^+ + e^- \leftrightarrow \text{Na}(\text{s}) \).

\[
E_{Na} = E_o + \frac{2.303RT}{F} \log([Na^+]) \quad (A.3)
\]

Finally, the chloride concentration-voltage relationship can be determined from the reaction \( \text{AgCl}(\text{s}) + e^- \leftrightarrow \text{Ag}(\text{s}) + \text{Cl}^- \).

\[
E_{Cl} = E_o - \frac{2.303RT}{F} \log([Cl^-]) \quad (A.4)
\]

Through calibration with solutions of known salinity and acidity, we can find the slope of the voltage shift per decade of concentration change (pH and pNa would be \( \sim -55 \text{ mV/decade} \) at room temperature, and pCl would be +55 mV/decade).

The premise of these measurements is straightforward. However, the challenge is that these are very sensitive voltage measurements that can be easily affected by
Figure A-1: Probe response to applied voltage across CDI cell in 1 mM NaCl.
noise. Therefore probes need high impedance, and the electric response has to be measured in a way that prevents leakage current from dominating the measurement. In our system, the pH probe had an enclosed reference, which in theory would have a high enough impedance to prevent current from flowing through. However, in practice we observed that the pH responded to applied voltages in the CDI cell, regardless of the magnitude of the voltage or in the presence of CNT electrodes or just a bare cell (Figure A-1). The sodium and chloride probes however were in line with a shared reference electrode, and we found that the signals interfered with one another. These responses imply that a ground loop current exists.

The CDI cell has a floating ground in order to prevent any limits of the current response. This means the solution has a floating ground. The probes were plugged into EDAQ Isopods (Figure A-2), which is designed for differential measurements by having an isolated ground and taking a differential measurement between the sensor and reference electrode. We found we could remove the ground loop between the Na and Cl probes by using a fluid valve to alternate taking Na or Cl measurements during a given cycle, physically preventing current flow in solution. However, the bigger challenge of lacking a solution grounding wire for the electrodes, meant that current could flow through the reference and shift the voltage unreasonably. Figure A-1 shows the probe response at the outlet either in-line with a bare flow cell (low surface area, minimal desalination), compared with VA-CNT in the CDI cell at varying voltages. Even in the bare cell, where there is little change in the solution conductivity, the pH fluctuates in response to an applied voltage, though at 1V we don’t anticipate
Figure A-3: Sample outlet pH readings with grounded probe. Desalination experiments for these three cells were presented in Chapter 4.

electrolysis. In addition, the sodium probe fluctuates by 50% while the conductivity does not, giving a false reading of desalination. Once VA-CNTs are loaded in the cell, we observe the typical changes in conductivity that suggest desalination. However, the pH goes to 9 during charging and to 4 during discharge. While this would not interfere with converting conductivity to NaCl concentration, it suggests there could be reactions in the cell. However, there is no voltage dependence on this response, and when comparing the effluent readings with pH paper we found strong disagreement (paper was consistently between 6-7). The sodium probe spikes by several orders of magnitude during charge/discharge, much greater than the concentration of ions in solution also suggesting a false reading. Finally, while the chloride probe has reasonable magnitude, the drift in the probe is quite high, making it difficult to determine absolute values of chloride concentration from voltage readings. The ground loop current can lead to many false readings and false conclusions. We recently tried to incorporate a grounded pH probe into the set up (we were unable to find grounded sodium and chloride probes). We found that the grounded pH probe does not seem to have large shifts in response to an applied voltage in the flow cell, and found good
agreement between the grounded probe and pH paper in readings. The sensor showed over the course of experiments some drift to more basic readings, but generally all experiments conducted in Chapter 4 (at 1.25V) yielded pH fluctuations between 5 and 8, suggesting protons are adsorbing or reacting at the carbon surface (Figure A-3). In addition, these pH values show that the conductivity readings are most affected by sodium and chloride desalination, and pH fluctuations are negligible.

In order to definitively eliminate ground currents, the sensors and solutions need to share the same ground. In order to do this, we recommend purchasing differential electrodes which are similar to the grounded electrode set up but also have a pre-amplifier built in (Figure A-4). The differential electrode still has the sensor, reference, and ground electrodes, but sends the signal to a pre-amplifier. The ground wire has low impedance and thus takes any current load. The pre-amplifier is used to subtract out that effect and leave us with a pristine differential electrode measurement between the sensor and reference. This signal could then be sent to the EDAQ isopod or other meters and be isolated. Thus, in order to take ion measurements careful set up of the sensors is needed, and in some cases commercial development of a pre-amplifier to convert the signal. In conclusion, a solution grounded electrode is better, but a differential electrode is best. For now, when using standard electrodes and signal amplifiers, we suggest researchers to compare signals when they allow fluid to flow while charging/discharging compared to charging with a valve closed, and then removing the electric field while flowing solution to physically prevent ground current flow.
Appendix B

VA-CNT Synthesis and Example Code

VA-CNTs were synthesized in a two-furnace set up, with a pre-heater and a growth furnace. The 1" tube furnaces were purchased from Thermo Scientific. Solenoid valves and flow-meters were used to control the flow of gases in the system: hydrogen, helium, ethylene, and water vapor (from a bubbler connected to helium). A sample growth script is provided below.
Listing B.1: VA-CNT Synthesis Code in Ansari

' Synthesis adapted from previous scripts in NECSTLab
' Doug Jacobs 6/13/2014
' From Alex 8/5/2013, stabilize H2 ramp, added delam, added water, shortened growth

' Cleaning the tube
set helium to 1000 sccm
turn helium on
wait for 4 min
set hydrogen to 200 sccm
turn hydrogen on

' Ramp to temperature, please turn on 0.7 bubble per second of water at ~600C (~0.01 scfh)
set helium to 37 sccm
set zone 1 to 200 degC
set zone 2 to 200 degC
turn zone 1 on
turn zone 2 on
wait for 4.5 minutes
wait until zone 1 temperature > 199 degC
set zone 1 to 740 degC
set zone 2 to 800 degC
turn zone 1 on
turn zone 2 on
wait until zone 1 temperature > 600 degC
set water to 5.4 sccm
turn water on
wait until zone 1 temperature > 738 degC
wait for 5 min

' Growing CNTs
set ethylene to 150 sccm
turn ethylene on
wait for 7.5 minutes
turn ethylene off
turn zone 2 off

'Delamination Process
set hydrogen to 250 sccm
wait 0.1 minutes
email hmutha@mit.edu with a message saying "time to open lid"
wait 1 minutes

' Shut down, please immediately open lid and turn off water
turn water off
turn hydrogen off
turn zone 1 off
set helium to 920 sccm
wait 10 minutes
set helium to 100 sccm
wait until zone 1 temperature < 180 degC
turn helium off
email hmutha@mit.edu with a message saying "CNT Growth Completed"
turn log off
Appendix C

Advection-Diffusion Model Code Implementation

A parametric sweep of Péclet number, electrode length scale ratio, and cycling frequency was conducted using MATLAB. The governing equations and results are given in Chapter 4. Attached here is the original code used in this thesis. The first function generates a parametric sweep file, while the simulation code can then load a set of parameters to run a CDI cell for specified $Pe$, $L_{rat}$, and $f^*$. 
Listing C.1: Parametric Sweep Table Generator

\initiates jobs for the frequency cycling study

```
foldernew=['frequency_with_outletconc'];
mkdir(foldernew)
Pe=logspace(-1.5,2.0,20); %Peclet=Q*Le^2/(B*lsp*lsp*Deff)
Lrat=[0.5, 1, 5, 10]; % Lrat = Le/Lsp
tau=[1];
tcycle_len=logspace(-2,4,7); %duration of half cycle
DutyCycle=0.5;
param_sweep=[0,0,0,0,0];
for Pes=1:length(Pe)
    for Lrats=1:length(Lrat)
        for ths2=1:length(tau)
            for ths=1:length(tcycle_len)
                for dcs=1:length(DutyCycle)
                    if Pe(Pes) < 1
                        tau_p = 1.0 / Pe(Pes);
                    else
                        tau_p = 1.0;
                    end
                    params_new=[Pe(Pes),Lrat(Lrats), tau_p, tcycle_len(ths), DutyCycle(dcs)];
                    param_sweep=[param_sweep;params_new];
                end
            end
        end
    end
end
fprintf('num params: %d
', size(param_sweep, 1));
save(fullfile(foldernew,'Parameters.mat'), 'param_sweep')
```

Listing C.2: Flow Cell Simulation for Varying Cycling Frequencies

```matlab
function []=FrequencySimulation(foldernew, zz)

load(fullfile(foldernew, 'Parameters.mat'))
P_e=param_sweep(zz,1);
Lrat=param_sweep(zz,2);
tau=param_sweep(zz,3);
tcycle_len=param_sweep(zz,4);
DutyCycle=param_sweep(zz,5);
incomplete_cycle=0;

%% properties
%
x spacing \%x goes from 0 to 1
dx=0.25;
xs=dx/2:dx:1; %located at centroid of element
Nx=length(xs);
%
electrode y spacing
dy=0.25;
ys=dy/2:dy:1; %located at centroid of element
Ny=length(ys);
%
Boundary layer thickness \{calculate for developing flow, otherwise its
%the spacer channel thickness
del=1.475.*(2/3)^(-1/3).*Lrat^(-1/3).*xs.(1/3);
del(del>=1/Lrat)=1/Lrat;
%
time choose dt based on stability of geometry (computational
%stability)
del_dx=del(1);
Ctime=(del_dx*dx)/(Pe*del_dx+Lrat*dx); %convection time
Dtime=dy^2/2; %diffusion time
if Dtime <= Ctime
   dt=0.9*Dtime;
else
   dt=0.9*Ctime;
end
%
ensure that time step is smaller than cycling frequency
if dt >.01*tcycle_len
   dt=0.01*tcycle_len;
end
%
clean up time
indices=floor(tcycle_len/dt);
Time=dt*indices; %time for a half cycle clean (no roundoff issues)
Ncyclehalf=16;
totalT=Ncyclehalf*indices+1;

if totalT>10^7
   Ncyclehalf=6
   totalT=Ncyclehalf*indices+1;
end

cycle_splitter=indices*[1:Ncyclehalf−1]; %index for discharge,charge,discharge
shift=round((DutyCycle−.5)*cycle_splitter(2));
```
cycle_splitter(1:2:end)=cycle_splitter(1:2:end)+shift;

%generate a flux array
Aconstant=1/(4*tau+tau*exp(-5));
tin=0:dt:5*tau;
if dt=tau
    charging=1/dt;
    discharging=1/dt;
else
    charging=Aconstant.*(-1+exp(-tิน./tau));
    discharging=Aconstant.*(-1-exp(-tin./tau));
end
zcharge=zeros(1,cycle_splitter(1)-length(charging));
zdischarge=zeros(1,(cycle_splitter(2)-cycle_splitter(1)+1)-length(discharging));
Ce_chargingprofile=[charging,zcharge];
Ce_dischargingprofile=[discharging,zdischarge];
Ce_add=[Ce_chargingprofile(1:cycle_splitter(1)),Ce_dischargingprofile(1:(cycle_splitter(2)-cycle_splitter(1)))];

%initialize array
Ce=zeros(Nx, Ny,2);%electrode
Ce(:,:,1)=0+Ce_add(1);%initialize charging
Cs=zeros(Nx,1,2); %spacer use for updating boundary condition
Cs(:,:,1)=0; %channel starts at bulk value
% initialize cycle counter
tt=1;
Cs_solution=zeros(10^7,2);
if totalT>10^7
    Cs_solution=zeros(totalT+1,2); %allot more space if needed upfront
end
while tt<totalT
    for ii=1:Nx
        dCedy=[(Ce(ii,1,1)-Cs(ii,1,1))/del(ii), diff(Ce(ii,:,1))./dy, 0];
        flux=-dCedy;
        d2Cedy=diff(dCedy)/dy;
        tadd=rem(tt,cycle_splitter(2));
        if tadd=0
            tadd=cycle_splitter(2);
        end
        Ce(ii,:,2)=squeeze(Ce(ii,:,1))+dt*(d2Cedy+Ce_add(tadd));
    end
    Ce(:,:,1)=Ce(:,:,2);%update the future as present
    Cs(:,:,1)=Cs(:,:,2);%update the future as present
    Cs_solution(tt,1:2)=[tt*dt,Cs(Nx,1,1)];
    if tt=totalT-1 %check that everything reached steady state otherwise add more cycles
        ci=cycicle_splitter(end-1)+1, cycle_splitter(end)]; %last cycle
        di=cycle_splitter(end+1, tt);
if Ncyclehalf<16
    ci0=[cycle_splitter(end−3)+1, cycle_splitter(end−2)]; %previous cycle
    di0=[cycle_splitter(end−2)+1, cycle_splitter(end−1)];
else
    ci0=[cycle_splitter(end−11)+1, cycle_splitter(end−10)]; %many cycles back
    di0=[cycle_splitter(end−10)+1, cycle_splitter(end−9)];
end

cequil=trapz(Cs_solution(ci(1):ci(2),1),Cs_solution(ci(1):ci(2),2));
dequil=trapz(Cs_solution(di(1):di(2),1),Cs_solution(di(1):di(2),2));

cequil2=trapz(Cs_solution(ci0(1):ci0(2),1),Cs_solution(ci0(1):ci0(2),2));
dequil2=trapz(Cs_solution(di0(1):di0(2),1),Cs_solution(di0(1):di0(2),2));
net=trapz(Cs_solution(ci0(1):di(2),1),Cs_solution(ci0(1):di(2),2));
if abs((cequil+dequil)/max(Cs_solution(di(1):di(2),2)))<10e−4
    analysis=1;
    break
elseif abs((cequil−cequil2+dequil−dequil2)/max(Cs_solution(di(1):di(2),2)))<dt^2
    analysis=1;
elseif length(Cs_solution)>10^7
    analysis=0; %throw away this run
    break
else
    Ncyclehalf=Ncyclehalf+6;
    totalT=Ncyclehalf*indices+1;
    cycle_splitter=indices*[1:Ncyclehalf−1];
cycle_splitter(1:2:end)=cycle_splitter(1:2:end)+shift;
end

filesavename=fullfile(foldernew, strcat('OutletConcentration_',num2str(zz−1)));
parsave(filesavename, Cs_solution, cycle_splitter);
if analysis==1 %solution has reached steady state, analyze final cycles
    tcharge=Cs_solution(ci(2),1)−Cs_solution(ci(1),1);
tdischarge=Cs_solution(di(2),1)−Cs_solution(di(1),1);
    Sadw=Pe/Lrat*trapz(Cs_solution(ci(1):ci(2),1),Cs_solution(ci(1):ci(2),2)); %adsorbed
    Sdes=Pe/Lrat*trapz(Cs_solution(di(1):di(2),1),Cs_solution(di(1):di(2),2)); %desorbed
tcycle=tcharge+tdischarge;
    Srate=Sads/tcharge;
    [Val,jj]=min(squeeze(Cs_solution(ci(1):ci(2),2)));
tpeak=Cs_solution(jj,1); %time to get to peak
    Cmax=Val;
cum=squeeze((cumtrapz(Cs_solution(ci(1):ci(2),1),Cs_solution(ci(1):ci(2),2))));
if incomplete_cycle==0 %find tcycle_99% if the cycling finished
    ii=find(abs(cum)/max(abs(cum))>0.99,1,'first');
    if isempty(ii)
        ii=length(cum);
    end
    tcycle99=Cs_solution(ii,1); %half cycle time
else
    tcycle99=NaN;
end
% Water Recovery Analysis
WR = (Sads/Pe) * Lrat / (tcharge);

% Phase shifting peaks
cum = squeeze((cumtrapz(Cs_solution(ci(1):di(2),1), Cs_solution(ci(1):di(2),2))));
[mpks, nloc] = max(cum); % local maxima
[npks, nloc] = min(cum); % local minima

Sads_phase = - (Pe / Lrat) * trapz(Cs_solution(ci(1)+mloc:ci(1)+nloc,1), Cs_solution(ci(1)+mloc:ci(1)+nloc,2));

if length((Cs_solution(ci(1)+nloc:di(2),1))) <= 1 % complete out of phase
    Sdes_phase = - (Pe / Lrat) * trapz(Cs_solution(ci(1):ci(1)+mloc,1), Cs_solution(ci(1):ci(1)+mloc,2));
else
    Sdes_phase = - (Pe / Lrat) * trapz(Cs_solution(ci(1):ci(1)+mloc,1), Cs_solution(ci(1):ci(1)+mloc,2)) -
                 (Pe / Lrat) * trapz(Cs_solution(ci(1)+nloc:di(2),1), Cs_solution(ci(1)+nloc:di(2),2));
end

WR_phase = (Sads_phase / Pe) * Lrat / (tcharge);
Srate_phase = Sads_phase / tcharge;
t_phase = Cs_solution(mloc,1);
solnew = [Pe, Lrat, tcycle_len, Sads, Sdes, Srate, MR, tcycle, tcycle99, tcharge, tpeak, Sads_phase, Sdes_phase, WR_phase, 
          Srate_phase, t_phase, incomplete_cycle, tau, DutyCycle];
else
    solnew = NaN(1,20);
end
solname = strcat('sol', num2str(zz));
parsave(fullfile(foldernew, solname), solnew, tcycle_len)
end
Appendix D

Summary of CDI experiments

The thesis presented numerous CDI experiments with varying geometries and setups. Here, we have summarized the set up and calculations for CDI cells discussed throughout the thesis, focusing on prototype 3 in Chapter 3 and the varying length scale ratios and duty cycle experiments presented in Chapter 4.

Table D.1: Summary of CDI experiments presented in Chapters 3 and 4

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<th>$C_\infty$ (mM)</th>
<th>Voltage (V)</th>
<th>$\Phi$ (mL/min)</th>
<th>$L_e$ ((\mu m))</th>
<th>$L_{sp}$ ((\mu m))</th>
<th>$D_e$ (10(^{-9}) m(^2)/s)</th>
<th>$L_c$ (cm)</th>
<th>$b$ (cm)</th>
<th>$Pe$</th>
<th>$L_{rat}$</th>
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