ELECTROLYTIC CAPACITIVE DISPLAY

by

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Abstract

This thesis describes the novel use of an electrolytic capacitor to controllably modulate the optical properties of a surface. The electrically-controlled modulation is achieved using electrodes comprised of carbon nanofoam, a new allotrope of carbon that has an extremely high surface to volume ratio, resulting in a very high capacitance per unit volume which enables the material to attract a significant amount of electrostatic charge, an amount that is much greater than would be the case if the electrodes were not so highly porous.

In the display described here, a diffusely reflective porous material, positioned above an interdigital array formed by two carbon nanofoam electrodes, was immersed in an electrolyte solution in which light-absorbing dye ions had been dissolved. When an electrical potential was applied across the electrodes, the capacitor charged and the dye ions were drawn into the pores of the electrodes and therefore drawn out of the bulk solution and porous material, causing the material to become reflective rather than colored. When the applied voltage was removed, the dye ions were able to diffuse out of the nanofoam and redistribute throughout the bulk solution and into the material, causing it to return to its original colored appearance. This effect was shown to be reproducible over many cycles and various experiments were conducted to develop a better understanding of the interaction of the dye ions with the carbon nanofoam electrodes and to understand how these interactions affect the time-course of the response.

Potential applications of this technology include low power, high-contrast reflective image display devices, particularly in applications where the visual appearance of ink on paper is required. These so-called “electronic paper” displays are becoming more common in devices such as e-book readers, but the displays that are currently used in these devices are limited in terms of brightness and switching speed. The results of this research indicate that this approach using high capacitance porous electrodes may have application in high contrast reflective display devices.
# Table of Contents

Abstract ............................................................................................................................... ii  
Table of Contents ............................................................................................................... iii  
List of Tables ..................................................................................................................... vi  
List of Figures ................................................................................................................... vii  
Acknowledgements ........................................................................................................... ix  
1 Introduction ................................................................................................................. 1  
2 Background ................................................................................................................. 3  
   2.1 Electronic Paper Displays .................................................................................... 3  
   2.2 Electrolytic Capacitors ......................................................................................... 8  
      2.2.1 Outer Helmholtz Plane - Capacitance ....................................................... 9  
      2.2.2 Inner Helmholtz Plane - Adsorption ....................................................... 12  
   2.3 Carbon Nanofoam .............................................................................................. 12  
   2.4 Ionic Mobility ..................................................................................................... 15  
      2.4.1 Electrophoretic Mobility ............................................................................ 15  
      2.4.2 Diffusion ................................................................................................... 17  
3 Electrical Control of Ion Concentration .................................................................... 19  
   3.1 Carbon Nanofoam Capacitance Measurements ................................................. 22  
      3.1.1 Carbon Nanofoam Capacitance Measurements in NaCl/H2O ............... 22  
      3.1.2 Carbon Nanofoam Capacitance Measurement in Brilliant Blue in Methanol ................................................................. 27  
   3.2 Adsorption of Methylene Blue on Carbon Nanofoam ....................................... 30  
   3.3 Ion Concentration Control Experiments ............................................................ 32
3.3.1 pH Concentration Change Experiment ....................................................... 32
3.3.2 Dye Concentration Control Experiment ..................................................... 35

3.4 Transmission vs. Time with Applied Voltage – Dye Concentration Measurements ....................................................................................................... 38

3.5 Conclusion .......................................................................................................... 42

4 Transmission Control Devices .................................................................................. 44

4.1.1 Description of Device ..................................................................................... 44
4.1.2 Description of Materials Used .................................................................... 46
4.1.3 Process for Filling Assembly ...................................................................... 48

4.2 Transmission Over Time with Applied Potential – Time Response Measurements ....................................................................................................... 50

4.3 Methylene Blue Mobility ................................................................................... 54
4.4 Electrochemical Reactions ................................................................................. 57
4.5 Conclusions ........................................................................................................ 59

5 A Reflective System ................................................................................................. 60

5.1 Description of Device......................................................................................... 61

5.2 Fabrication Techniques ...................................................................................... 66

5.2.1 Interdigital Carbon Nanofoam .................................................................... 66
5.2.2 Device Assembly ........................................................................................ 68
5.2.3 Materials ..................................................................................................... 69

5.3 Reflectance Changes in Response to Applied Potential Differences ................. 71

5.3.1 Experimental Reflectance Data ................................................................... 72
5.3.2 Images Depicting Reflectance Changes...................................................... 76

5.4 Diffusion Measurements .................................................................................... 77
5.4.1 Diffusion Measurements for Teflon® Filter ............................................... 77
5.4.2 Diffusion Rate for Carbon Nanofoam ......................................................... 82
5.5 Device Timing Predictions ................................................................................. 83
5.6 Conclusions ........................................................................................................ 86
6 Conclusion ............................................................................................................... 87
References .................................................................................................................... 89
Appendix A: Matlab Code used for Diffusion Simulation .............................................. 95
List of Tables

Table 3.1: Charge delivered and released from carbon nanofoam. ........................................... 28
Table 3.2: Experimental and theoretical capacitance values for carbon nanofoam. .............. 29
Table 3.3: Charge released from carbon nanofoam. ................................................................. 41
Table 4.1: Charge released from carbon nanofoam for transmissive display. ....................... 54
Table 5.1: Indices of refraction for relevant materials. ............................................................. 70
Table 5.2: Fresnel reflections. ................................................................................................. 71
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>A conventional polarizer-based liquid crystal display assembly</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>Basic scheme for electronic ink display</td>
<td>6</td>
</tr>
<tr>
<td>2.3</td>
<td>Outer Helmholtz plane</td>
<td>10</td>
</tr>
<tr>
<td>2.4</td>
<td>Several pieces of 254 µm thick carbon nanofoam cut into various shapes</td>
<td>14</td>
</tr>
<tr>
<td>2.5</td>
<td>Debye length for dissolved ions</td>
<td>16</td>
</tr>
<tr>
<td>3.1</td>
<td>Diffuse reflector electronic display</td>
<td>19</td>
</tr>
<tr>
<td>3.2</td>
<td>Basic schematic for interdigital electrodes</td>
<td>21</td>
</tr>
<tr>
<td>3.3</td>
<td>Front view of setup used for capacitance measurements</td>
<td>23</td>
</tr>
<tr>
<td>3.4</td>
<td>Experimental setup for carbon nanofoam capacitance measurements</td>
<td>24</td>
</tr>
<tr>
<td>3.5</td>
<td>Circuit diagram for electrolytic capacitor cell</td>
<td>26</td>
</tr>
<tr>
<td>3.6</td>
<td>Experimental setup for pH measurements</td>
<td>34</td>
</tr>
<tr>
<td>3.7</td>
<td>Brilliant blue dye concentration experimental setup</td>
<td>36</td>
</tr>
<tr>
<td>3.8</td>
<td>Vials with brilliant blue dye in methanol and toluene</td>
<td>37</td>
</tr>
<tr>
<td>3.9</td>
<td>Experimental setup for transmission measurements</td>
<td>38</td>
</tr>
<tr>
<td>3.10</td>
<td>Experimental setup for optical measurements</td>
<td>39</td>
</tr>
<tr>
<td>3.11</td>
<td>Brilliant blue concentration experiment transmission measurements</td>
<td>40</td>
</tr>
<tr>
<td>4.1</td>
<td>Transmissive display schematic</td>
<td>45</td>
</tr>
<tr>
<td>4.2</td>
<td>Assembly order for transmissive cell</td>
<td>49</td>
</tr>
<tr>
<td>4.3</td>
<td>Experimental setup used for transmissive display</td>
<td>50</td>
</tr>
<tr>
<td>4.4</td>
<td>Transmission measurements for transmissive display</td>
<td>52</td>
</tr>
<tr>
<td>4.5</td>
<td>Electrical schematic of carbon nanofoam capacitance</td>
<td>56</td>
</tr>
<tr>
<td>4.6</td>
<td>Fit for carbon nanofoam series resistor voltage (log scale)</td>
<td>57</td>
</tr>
</tbody>
</table>
Figure 5.1: Device schematic for reflective device, side view. ........................................ 61
Figure 5.2: Reflective device with potential applied across electrodes. ......................... 63
Figure 5.3: Reflective device from an aerial view. .................................................. 64
Figure 5.4: Experimental setup for reflective device .............................................. 65
Figure 5.5: Laser cutting pattern for interdigital carbon nanofoam electrodes .......... 67
Figure 5.6: Experimental setup for reflective device measurements ..................... 73
Figure 5.7: Reflective device reflection measurements ........................................... 74
Figure 5.8: Reflectance measurements for reflective device over many cycles ....... 75
Figure 5.9: Reflective device pictures cropped to only show Teflon® filter .......... 76
Figure 5.10: Diffusion measurements experimental setup. ................................... 78
Figure 5.11: Diffusion measurements experimental setup ................................. 80
Figure 5.12: Diffusion simulation grid system illustrated ....................................... 84
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1 Introduction

Since the emergence of the personal computer, the need for information displays has steadily increased. Conventionally these displays have worked by controlling the intensity of emitted light in pixelated patterns. However, emissive displays require substantial electrical power since they must generate their own light. In addition, emissive displays are not easily readable under bright ambient lighting. Now with the increasing popularity of portable electronics, the need for a low power, easily readable reflective information display that efficiently reflects ambient lighting is greater than ever. Electronic paper displays are a type of reflective display meant to meet this need.

Electronic paper displays have optical properties comparable to ink on paper, but with the convenience of electronic control. Current electronic paper displays have not yet taken advantage of the large market available due to their limited reflectance, which makes them unable to sufficiently recreate the visual effect of ink on paper\textsuperscript{1}. The technologies used in current electronic paper displays vary widely\textsuperscript{2}, which could be an indication of an absence of a clearly advantageous electronic paper technology. This thesis describes a new approach for creating an electronic paper display making use of high capacitance carbon nanofoam as an electrolytic capacitor that controls the ionic concentration within a white diffuser.

To begin, Section 2 of this thesis starts with a description of current electronic paper technologies. In addition, this section includes background details of the physics needed to understand this new approach, including electrolytic capacitors, carbon nanofoam, and electrophoresis.

Section 3 describes an experiment performed to demonstrate control of ion concentration by means of a carbon nanofoam electrolytic capacitor. The experiment involved placing two carbon nanofoam electrodes in two different solutions; one a solution of hydrochloric acid and the other a solution of a common type of dye in methanol and toluene. In both cases a voltage was applied across the device and the electrodes were capacitively
charged to reduce the ionic concentration and then discharged to replenish the initial concentration. The ionic concentration was measured using a pH meter in the hydrochloric acid and by measuring the transmission of a laser through the solution of dye ions in methanol and toluene. pH and transmission changes were then compared to expected values based on the capacitance of the carbon nanofoam.

Section 4 describes a device that used electrical control of ionic concentration to vary its transmission. The device used two pieces of carbon nanofoam with a solution of dye ions in methanol and toluene between them. The carbon nanofoam electrodes had holes through the center to allow light to transmit through. The transmission of a 635 nm laser through these holes was measured while different voltages were applied. The transmission changes and their dynamic characteristics were then compared to theoretical calculations.

Section 5 describes a device made using these same principles but which operates by means of variable reflectance. A porous diffuser was wetted with a solution of dye ions in methanol and toluene, and interdigital carbon nanofoam electrodes were placed adjacent to it, in the same solution. A voltage was then applied across these electrodes and the attraction of the ions into the nanofoam depleted the ion concentration of the solution in the diffuser. The reflectance of this diffuser was determined by measurements of the intensity of scattered reflected light from an incident laser beam. The reflectance and its dynamic characteristics were analyzed. Predictions for possible dynamic responses are discussed.

Section 6 presents the conclusions from this work. The optical characteristics of the transmissive and reflective devices are summarized and recommendations for applications of this new reflectance modulation approach are described.
2 Background

2.1 Electronic Paper Displays

The term electronic paper refers to a type of reflective display that has optical properties similar to that of ink on paper. They differ from emissive displays in that they reflect ambient lighting rather than emitting light from a built-in light source, which allows them to be read under even direct sunlight. Notable technologies of electronic paper involve conventional polarizer-based liquid crystals, cholesteric liquid crystals, electrophoresis of ink, electrofluidics, interferometric modulation, electrochromics, reverse emulsion electrophoresis and photonic crystals. This thesis is meant to describe and demonstrate an alternate technology for electronic paper.

Conventional reflective liquid crystal displays (such as the inexpensive ones that are used for calculators and digital watches) are currently the most well-established reflective display. The reflectance is controlled using liquid crystals between crossed-polarizers. A typical configuration of a liquid crystal display is shown in Figure 2.1.

The ITO electrodes shown in Figure 2.1 are patterned with small grooves. In the absence of an applied potential, these grooves cause the liquid crystal molecules to orient in the direction of the grooves. The liquid crystal molecules tend to align parallel to each other; hence when the grooves on the right-hand electrode are orthogonal to the grooves on the left-hand electrode, the liquid crystal molecules take on a helical structure. As polarized light passes through this structure, the helical structure rotates the polarization and allows light to transmit through the other polarizer. When a potential is applied between the electrodes, the liquid crystals instead align with the resulting applied electric field and do not rotate the polarization of incident light, causing incident light to be absorbed by one of the two crossed polarizers (or just the second polarizer if a polarized light source is used). A transmissive image display can be made by selectively applying the potential on a pixel-by-pixel basis, and illuminating the device with a backlight. Similarly, a reflective display can be made by placing a mirror at one end. In this configuration, the light that
transmits through the assembly will reflect back through the device in one mode, and will be absorbed by one of the two polarizers in the other mode.

Figure 2.1: A conventional polarizer-based liquid crystal display assembly. The liquid crystals tend to align with physical grooves on the indium tin oxide (ITO) surface creating a helical structure that rotates polarized light and allows light to transmit through the crossed polarizers.

This technology has been ineffective for electronic paper applications in part because they have low reflectance. The conventional liquid crystal display requires polarizers to work and hence when the displays are viewed under normal lighting conditions, the front polarizer absorbs 50% of incident light. This significantly restricts the maximum achievable reflectance. In addition, light incident on the display at oblique angles does not have its polarization rotated, meaning the reflective properties are highly angle dependent. A pocket calculator’s display, for example, appears much darker when viewed
along the surface of the display than it does when viewed directly. In contrast, paper has
diffuse reflectance characteristics, so the image is clearly visible when viewed from
different angles.

One specific type of liquid crystal, used in cholesteric liquid crystal displays (ChLCD),
may have some advantages over conventional liquid crystals for e-paper applications.
These liquid crystals tend to orient in a chiral structure (like the structure of DNA). The
device can reflect circularly polarized light of the same chirality within a narrow
wavelength band, and can be tuned to reflect a specific color of liquid. These displays are
bistable, meaning that no power is required to maintain the image. Companies producing
ChLCDs include Fujitsu, Hitachi, Kent Display, Kodak, Nemoptic, and ZBD Display.

The current most prominent electronic paper display technology uses controlled
electrophoresis of pigment particles to change reflectance. The most successful
technology of this type is manufactured by the company E-ink. Using light and dark
pigment particles with opposite electrostatic charge, the display works by electrically
moving these particles in and out of optical contact with the surface.

Figure 2.2 illustrates this principle. The display operates by controlling the reflectance of
small hollow capsules (typically 1-5 microns in diameter) that contain two different
colors of pigment particles. The electrodes on the viewing side must be transparent, and
indium tin oxide (ITO) is normally used for this reason. Based on the sign of the voltage
applied to these electrodes, the negatively charged white pigment particles are either
moved toward the transparent electrodes and into view, or away from the transparent
electrodes where they are hidden from view by the black pigment particles, in which case
the incident light is absorbed. By controlling the reflectance of each sphere, a pixilated
black and white display is created.
One problem with current electronic ink technology is its difficulty in controlling the movement of the pigment particles. Pigment particles have a tendency to flocculate and to stick to the surface of the microcapsules. As a result the applied potential needed to produce a desired reflectance in an individual pixel depends on the potential history of that pixel. If an applied potential were maintained across a microcapsule such that the white pigment particles are pulled to the surface, for instance, then the capsule would quickly appear white and slowly become lighter and lighter over time. If an opposite potential were then applied, the process would not happen in reverse. The display would quickly lose its white reflectance and then slowly appear darker. This means the potential required to change the reflectance of a pixel depends not only on its current reflectance,
but on the direction of change of reflectivity$^{14}$. This problem is called hysteresis, and is
difficult to eliminate even with sophisticated control algorithms.

Another technique used in electronic paper applications involves electrowetting of
liquids. Electrowetting technologies take advantage of surface energy effects in order to
move liquids by applying an electric potential. Liquavista$^{15}$, a manufacturer of displays
that use electrowetting technology, makes use of this approach through the use of a
highly reflective and hydrophobic surface placed adjacent to an interface between water
and immiscible colored oil. A hydrophobic surface has the characteristic that a drop of
water on the surface will bead up into a near spherical shape, in contrast to a hydrophilic
surface, in which water coats the surface in a thin flat layer. The characteristics of these
surfaces are a consequence of the surface energy relationships, and the application of an
electric field can control the degree to which a fluid will wet the surface. When an
electric potential is appropriately applied to the Liquavista display, the oil either spreads
out across the hydrophobic surface to create a colored, absorbing surface, or the water
wets the hydrophobic surface and the oil is pushed aside, revealing the reflective
substrate. The advantages of this technology are low power, wide viewing angle, and
video rate switching speed$^6$.

Interferometric modulator displays use a different technique based on interference of
light to create a reflective display. The display works by controlling the separation
thickness between two reflective plates. It has two stable states: one state in which the
separation between plates is set such that reflected light from each plate constructively
interferes for a given wavelength of light, and a second state in which the plates are
positioned such that visible light destructively interferes. Qualcomm MEMS
Technologies is currently the only company that has commercialized this technology$^7$.

Lastly, electrochromic displays make use of the color change of materials that undergo
electrochemical reactions. One example is a display that has light-absorbing dye ions
dissolved in a liquid, and positioned between two electrodes. When a potential is applied
across the solution, the dye molecules undergo a reaction that changes their absorption
properties. The reaction is reversible and hence a display can be made using pixelated
electrodes and transparent electrodes (typically indium tin oxide (ITO)). Electrochromics have the advantage of having a wide viewing angle and operating at low voltages, potentials as low as 0.25V. The disadvantage is that the time required to switch between the two states is long, typically 100 – 1000ms\(^8\). Companies currently working on electrochromic technology for display purposes include Acreo, Aveso, Ntera, and Siemens.

There are several additional technologies for electronic paper currently under development but not yet commercialized. Significant emerging technologies include, but are not limited to, reverse emulsion electrophoretic displays and photonic crystals.

2.2 Electrolytic Capacitors

An electrolytic capacitor is a capacitor consisting of two electrodes immersed in an electrolyte, which is a liquid containing dissolved ions. Each electrode acts as one side of a capacitor with the other side of the capacitor being the ions in the electrolyte. Electrolytic capacitors are important because they have an effective capacitor gap on the order of nanometers, which is much thinner than is practical with insulators, which are typically several orders of magnitude thicker. This very small capacitor gap enables much higher capacitances in some situations, including the device described in this thesis.

Specifically, when two conductive electrodes are placed in an electrolyte, a layer of ions around the electrodes are created. This layer is known as the electrical double layer, and is primarily composed of two separate layers. The outer layer of ions, known as the outer Helmholtz plane, comprises a similar charge density per unit area of electrode (and opposite sign) that interact with the electrode through long-range electrostatic forces, since the distances are typically larger than the radius of the molecule. The second layer, the inner Helmholtz plane, comprises cations, anions, and sometimes solvent molecules that interact with the electrode through short-range (on the order of the radius of the molecule) electrostatic forces\(^{16}\). In electrolytic capacitors, both layers are important in understanding its electrical properties.
2.2.1 Outer Helmholtz Plane - Capacitance

When two electrodes are placed into an electrolyte solution and a potential is applied between them, the cations and anions are attracted to opposite electrodes and begin to separate. In order for steady-state current to travel between the electrodes, electrical charge must physically traverse from one electrode to another, and in order for this to happen, the electrons from an electrode must be able to continuously free themselves from the cathode and become bound to a positively charged ion. The electron must also be able to free itself from the ion and become bound to the anode. Both processes require a chemical reaction to occur, which will occur if a well-defined energy barrier can be overcome. The size of the energy barrier is typically of order an electron volt. Such energy can be supplied by an applied potential, and typically it will be approximately:

$$E = q_e \cdot V$$  \hspace{1cm} (2.1)

In Equation 2.1, $E$ represents the maximum energy an ion has available to cause chemical reactions, $q_e$ represents the elementary charge and $V$ is the applied voltage across the electrodes in the electrolyte.

If the energy required for a chemical reaction is sufficiently greater than the available energy, then electrons cannot generally transfer between the ions and the electrode and hence there is no steady-state current. The ions will instead move near to the electrode surface. The closest these ions can get to the electrode surface is known as the outer Helmholtz plane. These ions will act as an opposite electrode of a capacitor. These capacitively bound ions distribute around the electrode in a three-dimensional region extending from the outer Helmholtz plane to the bulk solution.

The ions in this region distribute in such a way that the Coulombic attraction of the ions to an electrode is in equilibrium with the thermal agitation in the solution. It has been shown that the ionic concentration in this region then decreases with distance from the electrode\textsuperscript{16}. The ionic concentration is estimated to distribute in such a way that the potential within the bulk solution decays exponentially with distance from the electrode with a characteristic length known as the Debye length\textsuperscript{17}. The Debye length represents
the characteristic length of the decay of the electric field and is a property of the electrolyte solution. Typical Debye lengths for electrolytes are on the order of a few nanometers.

![Figure 2.3: Outer Helmholtz plane. The negatively charged ions and positively charged anions are dissolved in a solvent. When a potential is applied across the electrodes in this solvent the ions are attracted to the surface of the electrodes.](image)

The Debye length for a given electrolyte solution can be estimated using Equation 2.2\textsuperscript{17}.

\[
D = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2q_e^2 I}}
\]  
(2.2)
In Equation 2.2, $\varepsilon_o$ is the electrical permittivity of free space, $\varepsilon_r$ is the relative electrical permittivity of the solution, $k_b$ is Boltzmann’s constant, $T$ is the temperature, $q_e$ is the charge of an electron, and $I$ is the ionic strength (in ions/m$^3$).

In this situation in which a voltage of less than the energy needed for chemical reactions is applied across two electrodes in an electrolyte solution, the outer Helmholtz plane resembles a parallel plate capacitor with surface area equal to the surface area of the electrode and plate separation approximately equivalent to the Debye length. The standard formula for the capacitance of a parallel plate capacitor is given by Equation 2.3.

$$C = \frac{\varepsilon_o \varepsilon_r A}{\lambda_D} \quad (2.3)$$

In Equation 2.3, $C$ is the total capacitance of the two electrode system, $\varepsilon_o$ is the electrical permittivity of free space, $\varepsilon_r$ is the electrical permittivity of the solution between the plates, $A$ is the surface area of one electrode, and $\lambda_D$ is the separation between parallel plates. In the case of an electrolytic capacitor this distance is approximately the Debye length.

In reality, since each electrode has an oppositely charged ionic layer next to its surface, it acts as a capacitor. It requires two electrodes to apply a potential, so there are always two capacitors in series in an electrolytic capacitor. This means that the measured capacitance of an electrolytic cell will be one half of the capacitance of each individual electrode if the electrodes are equivalent in size and composition.

Finally, the surface area in Equation 2.3 does not represent the overall macroscopic dimensions of the electrode but rather the total effective surface area of the electrode. For a porous metal, for example, this surface area can be orders of magnitude larger than the macroscopic dimensions of the metal. The entire surface area contributes to capacitance in this case as long as the pore sizes are much larger than the Debye length in the electrolyte. If the pore sizes of the electrode are smaller than the Debye length, then there is not enough space for ions to travel into the pores and hence these pores will not contribute significantly to the total capacitance. This means that, in general, an
electrolytic capacitor that uses electrodes with a high effective surface area will have a larger capacitance than that of an electrolytic capacitor that uses solid metallic electrodes.

2.2.2. Inner Helmholtz Plane - Adsorption

In addition to the layer of ions surrounding an electrode at an applied electric potential, there is a second layer of molecules bound to the surface of the electrode. Unlike the outer Helmholtz plane, this layer of molecules does not generally have a net charge. The distance between the electrode and inner Helmholtz plane is also generally much smaller than that of the outer Helmholtz plane. Molecules bound to the electrode in this way are said to be specifically adsorbed. These bonds involve close-range forces which depend heavily on the chemical species involved. To further complicate matters, the adsorption of ions can either increase or decrease the rate of chemical reactions on the electrode surface, depending on certain conditions.

For the purposes of the experiments in this thesis, the chemical reactions have not been studied in depth. However, adsorption plays an important factor in controlling the ionic concentration of a solution. If an electrode adsorbs ions in a solution, then the ionic concentration will depend on the electrode’s adsorption capacity.

2.3 Carbon Nanofoam

For the electrolytic capacitors required for the experiments performed in this thesis, a conductive material with a very large capacitance was required. A mesh of small fibers in electrical contact would have been the ideal material to use because it would have a very large surface area while still having very large pores for the ions to traverse through. Carbon nanofoam is a material that has a similar structure and is readily commercially available, so this was selected for use in these experiments.

Carbon nanofoam is an allotrope of carbon first created in 1999 using a laser ablation technique. It has high conductivity despite relatively low density. The density of carbon is 2.267 kg/m³ while the density of typical carbon nanofoam is roughly 0.8 kg/m³. Since
the nanofoam is made of pure carbon, it is only about 35% carbon by volume. The structure is basically a foam of nanometer size-scale carbon fibers (commonly about 60nm in diameter). Due to the size scale and number of the fibers, the material has an extremely high surface area to volume ratio, typically of order 1,000,000.

The main reason the foam of fibers has such high capacitance is due to the small size-scale of the fibers. Consider a solid sheet of material with dimensions 3.35cm by 4.33cm by 76µm (dimensions similar to that of a piece of paper). The surface area per unit volume is easily calculated to be 26,315 m⁻¹. A cylindrical tube of radius 30nm, on the other hand, has a surface area to volume ratio of $6.7 \cdot 10^7$ m⁻¹. This means that if a rectangular mesh of cylindrical tubes was created that was 35% filled with tubes, 65% air; it would have almost 1,000 times more surface area than a solid piece of metal of the same dimensions. From Equation 2.3, the capacitance is directly proportional to the surface area. Hence 1,000 times more surface area means one would expect about 1,000 times more capacitance. This is why carbon nanofoam is ideal for use as an electrolytic capacitor; it essentially is mesh of thin, cylindrical rods.
Carbon nanofoam is also convenient to work with. It is non-toxic and is easy to cut but not brittle, so it can be formed into customized shapes. Figure 2.4 shows pieces of carbon nanofoam cut into various patterns.

One drawback to using carbon nanofoam as an electrolytic capacitor is its extremely high adsorptive capacity. Activated carbon, essentially a carbon powder, has the highest relative adsorptive capacity known to man\textsuperscript{23}. For this reason, it is used to filter liquids, including drinking water. Carbon nanofoam has essentially the same adsorptive properties and hence adsorbs most electrolytes in a solution. Therefore this must be carefully accounted for when carbon nanofoam is used as an electrolytic capacitor.
2.4 Ionic Mobility

The movement of ions in a solution can be characterized by two processes. The first is electrophoresis, which is the movement of ions in an electric field. The second is diffusion, which is the migration of ions from regions of high ionic concentrations to regions of low concentrations. The time required for an electrolytic capacitor to charge depends upon the speed at which the ions move through the electrolyte for a given applied potential, and this speed depends on the electrophoretic mobility of the ions. When the potential is removed, the time required for the ionic concentration in an electrolyte to become uniform depends on the diffusion coefficient of the ions in the electrolyte. When the electrodes of the same capacitor are electrically connected to one another, or in other words the device is shorted, the capacitor discharges and the ions migrate back into the solvent, so the diffusion rate is the key parameter in this process.

2.4.1 Electrophoretic Mobility

Some molecules, when placed in a solvent, will dissociate into positive and negative ions. In such cases, this is caused by the dipole nature of the solvent molecules overcoming the electrostatic attraction between the ions. The ions stay dissolved because of a small surrounding layer of solvent molecules that act to shield the electric field. The radius of this spherical shell around the ion is known as the Debye length.$$^24$$
Figure 2.5: Debye length for dissolved ions. In this case an ionic compound has dissolved in water, thus the ions are no longer ionically bound to one another. The water molecules align their dipole moments with the electric field from the ions and act to substantially shield the field beyond a characteristic length equal to the Debye length.

Figure 2.5 depicts two ions dissolved in a solution of water. A layer of water molecules forms around the charges and shields the field of the charge from the bulk of the solution beyond a characteristic shielding distance equal to the Debye length. Coulombic attraction between the positively charged ion and negatively charged oxygen atoms in each water molecule causes the oxygen to be attracted towards the positive ion and the positively charged hydrogen to be repelled away.

The resulting distribution of charge associated with the solvent and ion approaches electrical neutrality at distances much larger than the Debye length. However, the integrated net charge is not zero, so when a potential is applied between electrodes in an electrolytic capacitor, the positive ions will move toward the negative electrode and the negative ions toward the positive electrode, pulling the sphere of solvent with them. The associated drag on the ions is approximately proportional to the cross sectional area of the solvent sphere around the ion.
The rate at which the charges move under an applied potential is proportional to the electric field, with the constant of proportionality called the electrophoretic mobility. In the case of a charged particle with a radius less than the Debye length, as is the case for most ions, it has been shown that the electrophoretic mobility of the charge is determined by Equation 2.4:

\[ \mu_e = \frac{\varepsilon_0 \varepsilon_r \varphi_0}{\eta} \] (2.4)

In Equation 2.4, \(\varepsilon_0\varepsilon_r\) is the electrical permittivity of the medium, \(\eta\) is the dynamic viscosity of the medium, and \(\varphi_0\) is known as the zeta potential.

As an ion moves through a liquid, some solvent molecules are pulled along with the ions while solvent molecules at distances much larger than the Debye length are not. The double layer potential, also known as the zeta potential, is the potential at the distance from the ion where the solvent molecules no longer move with the ion\(^2\). The zeta potential cannot be measured directly and actually needs to be calculated from measurements of the electrophoretic mobility. Since no electrophoretic mobility data is available for the electrolytes used, a zeta potential of 25 mV was estimated based on common zeta potentials for similar solutions\(^3\).

To summarize, the speed with which an ion travels through a medium in an electric field is the product of its electrophoretic mobility and the electric field, as per Equation 2.5:

\[ \vec{v} = \mu_e \cdot \vec{E} \] (2.5)

### 2.4.2 Diffusion

The second process governing ion transport is the movement of ions from regions of high ionic concentrations to regions of low concentration. This process is important for the electrolytic capacitive display described in this thesis because it is the primary mechanism by which ions move through the device.
The ions in a liquid have an average speed depending on the temperature of the liquid. The direction of their velocity changes randomly. If the concentration of the ions is not uniform throughout the liquid, then the random direction of the ions will eventually cause the concentration to become uniform. In order to estimate the rate at which this happens, one needs to calculate the diffusion current\textsuperscript{28}.

\[
J_x = -D \cdot \frac{dn}{dx} \tag{2.6}
\]

In Equation 2.6, $J_x$ is the diffusion current in a given direction in units of molecules/(m\textsuperscript{2}·s), $D$ is known as the diffusion constant, and $dn/dx$ is the concentration gradient in the direction of molecular current. The diffusion current in a given direction is essentially the number of molecules that pass through a unit cross sectional area in a unit time. The diffusion constant thus has units of m\textsuperscript{2}/s and is determined by the mean free path of a particle in the fluid and its average speed.
3 Electrical Control of Ion Concentration

The approach described in this thesis for producing electronic paper requires electrically controlling the motion of light absorbing particles. However, rather than moving relatively large pigment particles (roughly 840nm in diameter) as described in the previous section, far smaller dye ions, typically 1nm in diameter\textsuperscript{29}, are employed. The advantage of dye ions is that, because they are much smaller, they do not flocculate and do not suffer from hysteresis problems. The display contemplated in this work operates by controlling the reflectance of a diffusely reflective material, as shown in Figure 3.1. A diffusely reflective material, referred to here as the diffuser, reflects incident light over a wide range of angles.

![Diffuse reflector electronic display](image)

Figure 3.1: Diffuse reflector electronic display. The display works by controlling the light absorbing properties of a reflective diffuser. Small circles represent light-absorbing dye ions, significantly enlarged for illustrative purposes. Counter-ions do not generally affect light and are thus not shown.
Paper, for example is a diffuser that has high reflectance as a result of its high porosity. Incident light is scattered by the fibers in the porous mat of the paper and reflects in random directions. The diffuser used in this thesis, a highly porous Teflon® filter, has physical properties very similar to paper in order to recreate its optical properties. It was used because it has an even higher porosity than paper and is even more reflective, which was necessary when the material was immersed in a solvent. When immersed in a transparent liquid, such that the pores are completely filled with the liquid, this diffuser was highly reflective with optical properties similar to that of paper. When the diffuser was immersed in a solution of light-absorbing dye ions in a solvent, the dye ions in the pores of the diffuser absorbed the incident light and reduced reflectance, causing a dark appearance.

In order to control reflectance, a structure of alternating, interdigital carbon nanofoam electrodes were placed adjacent to this diffuser. Interdigital electrodes are electrodes that interweave like fingers, designed to minimize the distance from any given ion to an electrode of high or low potential. A diagram of interdigital electrodes is shown in Figure 3.2.

When an electrical potential, typically a few volts, is applied between these electrodes, they attract the dye ions out of the diffuser’s pores and capacitively store them. When the electrodes are electrically connected to one another, the capacitor discharges and the dye ions diffuse back into the diffuser creating an absorptive, dark appearance.
In contrast to electronic ink displays that involve moving large pigment particles (of order 800nm in diameter), the method for an electronic paper display described in this thesis involves moving much smaller dye ions (of order 1nm in diameter) via the charging of an electrolytic capacitor in which the ionic solution is the electrolyte. Controlling the concentration of dye ions adjusts the degree of light absorption and, because of their small size, do not have the flocculation and hysteresis problems observed with pigment particles. In order to use dye ions, however, far more charge needs to be moved in order to achieve a comparable change in reflectance since the absorption per unit charge is much less than for pigments. Extremely high capacitance is required. This section describes how sufficient capacitance can be achieved through the use of carbon nanofoam as the electrodes of an electrolytic capacitor.
A potential was applied to carbon nanofoam electrodes, which caused the ions in the solution to be pulled into its pores. This section begins by describing the methods used to experimentally verify this effect and ends by analyzing the measured results. Section 3.1 describes an experiment in which the capacitance of the carbon nanofoam was measured in order to establish that the carbon nanofoam could store a sufficient amount of charge. We found that carbon nanofoam has a strong adsorptive capacity and that this adsorption needed to be prevented, and Section 3.2 describes a method for doing so. Lastly, this section describes a demonstration of ionic concentration control. Section 3.3 describes an experiment demonstrating reversible pH changes in hydrochloric acid and Section 3.4 describes an experiment demonstrating an optical transmission change through a solution of a particular ionic dye, brilliant blue, in water.

3.1 Carbon Nanofoam Capacitance Measurements

The carbon nanofoam capacitance was measured in a 6.1 moles/liter solution of NaCl in water and a 1.76·10^{-3} moles/liter solution of brilliant blue in methanol. The NaCl solution was chosen to represent a typical highly concentrated electrolyte solution. The brilliant blue in methanol solution was chosen to be typical of a dye in a common solvent. The two subsections of this section detail each measurement and compare results to values provided by the carbon nanofoam supplier.

3.1.1 Carbon Nanofoam Capacitance Measurements in NaCl/H₂O

For the measurements, two pieces of carbon nanofoam with dimensions 20mm by 5.0mm by 250µm thick were submerged in a 6.1 moles/liter NaCl/water solution. The salt water solution was contained in a cylindrical beaker that was 3cm tall and had a diameter of 7.5cm and was filled with 130ml of salt water. A 300mV voltage was applied across the two electrodes. The voltage across a 47Ω resistor in series with the electrodes was measured to determine the current passing between the electrodes. A data acquisition system recorded the voltage across the resistor over time. When the voltage on the series
resistor fell to zero, the carbon nanofoam electrodes were fully charged. The voltage across the series resistor was then integrated over time to determine the total amount of charge in the electrodes.

The capacitance of the carbon nanofoam setup was measured experimentally using the setup shown in Figure 3.3 and 3.4.

![Diagram of capacitance measurement setup](image)

**Figure 3.3:** Front view of setup used for capacitance measurements. Two carbon nanofoam electrodes are submerged in NaCl in water. The voltage across a series resistor is measured while the nanofoam is charged and discharged.

The dimensions of the submerged carbon nanofoam pieces were 250µm thick and 20mm by 5.0mm, resulting in a volume of $2.5 \cdot 10^{-8}$ m$^3$ each. The separation between the carbon nanofoam was 5mm. The separation was set to be as small as was practical while still being large enough to ensure the electrodes were not in electrical contact. This spacing did not affect capacitance, as the capacitance between the electrodes in an electrolytic capacitor is determined by the Debye layer rather than the distance between the
electrodes. However, the initial electric field in the solution between the electrodes is determined by the applied potential divided by the separation distance, so the spacing may affect the charging rate because the speed of the ions through the electrolyte is proportional to the electric field (see Section 2.4.1).

As shown in Figure 3.3, metallic clamps were used to hold the carbon nanofoam electrodes in place and to make electrical contact with the carbon nanofoam. In this case, two separate Third Hand Adjustable Parts Holders that were electrically isolated from one another were used to hold each piece. The Third Hand holder used alligator clips with sharp metallic teeth that had a tendency to break the nanofoam due to the high localized pressure, so two flat pieces of stainless steel of dimensions 5mm by 5mm by 2mm thick were inserted between the teeth of the alligator clips on each side of the nanofoam to distribute the force across the nanofoam and prevent damage. Stainless steel

**Figure 3.4: Experimental setup for carbon nanofoam capacitance measurements.**
This side view shows a third hand holder holding the nanofoam in place in the salt water. Stainless steel plates are placed between the nanofoam and alligator clips to distribute the force across the nanofoam.
was used because it is electrically conductive but, unlike other metals (e.g., aluminum), it does not form an impermeable non-conductive oxide layer in air.

Next, a 0.2V potential difference was applied between the Third Hand Holders with a Circuit-Test PS5030-D 30V 5A Power Supply. The total current that passed across the electrodes was measured using a series resistor of 47Ω. The total charge on the electrodes after charging was calculated by integrating the current across the series resistor over time (in reality, because of the discrete data acquisition process, this was a sum).

$$Q = \sum \frac{V_i \cdot \Delta t}{R}$$  \hspace{1cm} (3.1)

Using Equation 3.1, the voltage measured across the series resistor, $V_i$, at a given time was multiplied by the sampling period, $\Delta t$, and divided by the series resistance, $R$, to find the total amount of charge that passed through the series resistor during the time $\Delta t$. These values were summed to calculate the total charge capacitively charged on the carbon nanofoam, $Q$.

After applying a 200mV potential difference across the electrodes for four minutes, the total charge on the electrodes was determined to be $(32 +/- 1)\text{mC}$. After discharging for four minutes, the total charge discharged from the carbon nanofoam was measured to be $(26 +/- 1)\text{mC}$. The discrepancy between the total amount charged and the total amount discharged indicated that not all the current through the series resistor represented ions being capacitively stored on the nanofoam. This was an indication that there was a mechanism for charge transfer between the carbon nanofoam electrodes other than through the series resistor. This can be considered to be equivalent of a conductive mechanism that can be modeled as a resistor in parallel with the capacitance of the cell. A circuit diagram of the system with the internal resistance included is shown in Figure 3.5.
To calculate the capacitance of the carbon nanofoam, the total amount of charge that passed through the series resistor during the discharging phase was determined and this value was divided by the applied voltage. The charge measured during the discharging phase was used so that any current that travelled via the alternate conductive mechanism would not be counted. This was done so that if the measured capacitance was sufficiently high, then the capacitance of the carbon nanofoam would be shown to have enough capacitance to be a feasible option for the electronic paper display. The measured capacitance for the carbon nanofoam was 130mF. The total capacitance per unit volume of the two electrode carbon nanofoam device was found to be $(2.6 \pm 0.3) \cdot 10^6$ F/m$^3$.

Theoretically, one would expect the capacitance of the carbon nanofoam to be related to its surface area and the Debye length in the electrolyte solution, as shown in Equation 2.3. The surface area of the carbon nanofoam used was purported by the supplier to be $400 \text{m}^2/\text{g}$ and the density was $450 \text{kg/m}^3$. The estimated surface area of the carbon
nanofoam was found by multiplying the density, surface area per weight, and volume of carbon nanofoam used in the experiment. The estimated surface area was $(0.46 \pm 0.09) \text{m}^2$.

The Debye length can be estimated using Equation 2.2. For water, the relative permittivity is $80.0^{31}$ and the ionic concentration used in the experiment was $3.70 \cdot 10^{27}$ molecules/m$^3$. The Debye length was thus estimated to be $(1.23 \pm 0.01) \cdot 10^{-10}$ m.

The predicted capacitance of the carbon nanofoam, using the parallel plate approximation from Equation 2.3, is $1.3 \text{F}$. In comparison, the measured value of $130 \text{mF}$ for the carbon nanofoam was approximately 10% of this predicted value. A possible explanation for this discrepancy is that the entire surface of the carbon nanofoam was not being capacitively charged.

### 3.1.2 Carbon Nanofoam Capacitance Measurement in Brilliant Blue in Methanol

The capacitance of the carbon nanofoam was also measured for brilliant blue in methanol. A setup similar to that shown in the previous section in Figure 3.1 was used with the NaCl in water solution replaced with 1.5g/L brilliant blue in methanol.

The total volume of the both carbon nanofoam electrodes submerged in the solution was $(5.0 \pm 0.4) \cdot 10^{-8}$ m$^3$. The applied potential in this case was 100mV. Once again the capacitance was measured by integrating the charge across the series resistor during the discharging phase. This was done three times in order to estimate the reproducibility of the capacitance. The measured charges for all three trials deviated less than the expected measurement uncertainty during both the charging and discharging phase. The total amount of charge transferred during these cycles was:
Charge transferred to carbon nanofoam under 0.1 V applied potential

<table>
<thead>
<tr>
<th>Trial</th>
<th>Charge transferred</th>
<th>Charge discharged</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-(1.33 +/- 0.08)·10^{-2} C</td>
<td>(7.8 +/- 0.6)·10^{-3} C</td>
</tr>
<tr>
<td>2</td>
<td>-(1.11 +/- 0.08)·10^{-2} C</td>
<td>(8.3 +/- 0.6)·10^{-3} C</td>
</tr>
<tr>
<td>3</td>
<td>-(1.02 +/- 0.08)·10^{-2} C</td>
<td>(8.1 +/- 0.6)·10^{-3} C</td>
</tr>
</tbody>
</table>

Table 3.1: Charge delivered and released from carbon nanofoam. Applied potential difference was 0.1 V during the charging phase and 0 V during the discharging phase.

The capacitance for the two electrode system was calculated using the average amount of charge discharged from the carbon nanofoam. The capacitance was estimated to be $8.1 \times 10^{-2}$ F. The Debye length of the carbon nanofoam in the brilliant blue in methanol solution was estimated using Equation 2.2 with a relative permittivity of methanol of 32.6$^{27}$, and an ionic concentration of $1.094 \times 10^{24}$ molecules/m$^3$, yielding a value of $(4.56 +/- 0.05) \times 10^{-9}$ m.

Based upon this estimated Debye length and the surface area of carbon nanofoam of 0.46 m$^2$, the expected capacitance using the parallel plate capacitor approximation is $1.5 \times 10^{-2}$ F. Surprisingly, the measured capacitance was more than five times this value. This suggests that the parallel plate capacitance approximation may not be a dependable approximation.

The company that supplied the carbon nanofoam, Marketech International, quoted the capacitance of the carbon nanofoam to be $7.65 \times 10^6$ F/m$^3$ for a two electrode system. For comparison, we divided our measured capacitance by the volume of the carbon nanofoam, however the relevant Debye length was not specified, so this value has unknown usefulness here.
A summary of the measurements and calculations from this section are shown in Table 3.2. The experimentally measured capacitance of the carbon nanofoam in a highly concentrated solution of NaCl in water was found to be $(2.6 +/- 0.3) \times 10^6 \text{ F/m}^3$. The capacitance for a moderately concentrated solution of brilliant blue dye in methanol was found to be $(1.60 +/- 0.3) \times 10^6 \text{ F/m}^3$. In the case of NaCl in water the measured capacitance was significantly less than the expected capacitance using the parallel plate approximation. The capacitance measurement for brilliant blue in methanol was higher than the value estimated using the parallel plate approximation. This suggests the parallel plate approximation may not always be a reliable tool for estimating capacitance in such a system. For the work in this thesis, the experimental capacitance values found for brilliant blue in methanol will be used. Both measured capacitance values were significantly less than the manufacturer’s specified capacitance of $7.65 \times 10^6 \text{ F/m}^3$, but the correlation to the manufacturer’s specification is unclear as the methods the manufacturer used to measure capacitance are not known. Both measured capacitance values were within an order of magnitude and in this situation, for this purpose, it was concluded that the carbon nanofoam was working sufficiently well for the purposes of ionic concentration control.

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Parallel Plate Approx.</th>
<th>Manufacturer’s Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl in Water</td>
<td>$(2.6 +/- 0.3) \times 10^6 \text{ F/m}^3$</td>
<td>$(2.6 +/- 0.5) \times 10^7 \text{ F/m}^3$</td>
<td>$7.65 \times 10^6 \text{ F/m}^3$</td>
</tr>
<tr>
<td>Brilliant blue in methanol</td>
<td>$(1.60 +/- 0.3) \times 10^6 \text{ F/m}^3$</td>
<td>$(3.0 +/- 0.3) \times 10^5 \text{ F/m}^3$</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Experimental and theoretical capacitance values for carbon nanofoam.
3.2 Adsorption of Methylene Blue on Carbon Nanofoam

Although the capacitance of the carbon nanofoam was measured to be sufficient for ionic concentration control, as noted in Section 2.2.2, there is an additional important factor to consider: the short-range electrostatic attraction between the ions and the carbon. For many ions, this attraction is strong enough to overcome solubility effects, which causes ions to bond directly to the carbon surface, an effect often called adsorption. The extremely high surface area of carbon nanofoam results in a high adsorptive capacity. This characteristic complicates experiments using carbon nanofoam electrodes in electrolytes. Therefore it was desirable to find a stable electrolyte solution in which the ions do not absorb to the carbon nanofoam to a problematic extent.

A simple experiment was performed to determine which dyes absorb to carbon nanofoam. Single pieces of carbon nanofoam of dimensions 250µm thick, 2cm long and 0.5cm wide were placed in vials containing 4ml of various dyes in methanol. Dyes used included brilliant blue, napthol black, violamine R, as well as methylene blue. The concentrations of dyes used were 0.05 g/L, corresponding to molarities ranging from $1.5 \times 10^{-4}$ to $0.5 \times 10^{-4}$ moles/liter. The vials containing dye solution were then sealed to ensure that there were no chemical reactions occurring between the carbon nanofoam and the dye solution as a result of exposure to the ambient air. The carbon nanofoam was also electrically connected to ground via a thin metal wire adhered using a conductive silver epoxy. This was to ensure that there was no electrical potential difference between the nanofoam and ground. The setup was then left overnight. Initially the dye solutions were colored; however after 24 hours with carbon nanofoam the solutions were visibly transparent. Transmission through the vials was not measured since the transmission changes were dramatic enough to be clearly visible by eye.

In order to create a stable ionic concentration with a carbon nanofoam electrode present in the solution, it was necessary to either use an electrolyte that does not adsorb to carbon nanofoam or to saturate the adsorptive capacity of the carbon nanofoam prior to conducting the experiment. A literature search into compounds that adsorb to activated
carbon did not find any dyes that did not adsorb, however activated carbon was found to have a particularly high adsorptive capacity for the solvent toluene$^{32}$ and we hypothesized that if the toluene molecules were to coat the carbon surface, this might prevent adsorption of dye ions. Unfortunately, most dyes are not soluble in toluene. However, since methanol is miscible in toluene, we postulated that a solution of dye ions dissolved in methanol and mixed with toluene might work. We tried the same concentration of dye solutions described above, but this time using a solvent of 50% methanol and 50% toluene by volume. The adsorption experiments described above were repeated using these new solutions and no visible color change was observed for any of the dye solutions. To our knowledge, this is the first use of toluene to impede adsorption of ionic dye ions in carbon nanofoam.

To confirm that the amount of toluene present was sufficient to saturate the adsorptive capacity of carbon nanofoam, the adsorptive capacity was estimate for activated carbon. Activated carbon has an adsorption capacity for methylene blue estimated to be 40% of its weight$^{32}$. The adsorption capacity of toluene is also estimated at 40% of its weight$^{32}$. The density of toluene is 865 kg/m$^3$,$^{33}$ nearly twice that of the carbon nanofoam. Thus, in order to have enough toluene present to saturate the adsorptive capacity of the carbon nanofoam, the weight of the toluene present needs to be at least 40% of the weight of the carbon nanofoam. Thus, in terms of volumes, the volume of a 50% toluene/50% methanol solution needs to be at least that of the carbon nanofoam, a condition that was easily met.

As an additional safeguard to prevent adsorption, we felt it was advisable for the concentration of toluene to be much larger than the concentration of dye ions in the solution. Otherwise if, for instance, the concentration of toluene molecules and methylene blue ions were the same, then the carbon nanofoam might adsorb comparable amounts of both molecules. In a solution of methylene blue ions having a saturation-limited concentration in a solution of equal amounts toluene and methanol, the ionic concentration would be $1.41 \cdot 10^{25}$ molecules/m$^3$.$^{34}$ This same solution would have a concentration of toluene molecules equal to $2.827 \cdot 10^{27}$ molecules/m$^3$.$^{35}$ Thus the
solution has a concentration of toluene molecules that is 200 times higher than the ionic concentration of methylene blue.

In summary, the adsorption of dye ions onto the carbon nanofoam can be prevented as long as the volume of the solution (assuming 50% methanol, 50% toluene by volume) is at least as large as the volume of the carbon nanofoam used. In addition, the concentration of toluene needs to be much larger than the ionic concentration of the electrolyte. We were encouraged that both of these requirements are readily fulfilled.

### 3.3 Ion Concentration Control Experiments

With sufficient capacitance, the ionic concentration of a solution can be continuously changed using an electrolytic capacitor immersed in the solution. In addition to controlling the optical properties of a dye solution, ionic concentration control has another interesting application. For a solution of non-neutral pH, the pH can be continuously controlled using a method similar to that used for dye concentration control. In the following experiments, the ionic concentration of a solution of HCl in H₂O and brilliant blue dye in methanol and toluene were reproducibly changed by inserting two carbon nanofoam electrodes into the solution and applying a potential difference between them to demonstrate ionic concentration control for two different applications.

#### 3.3.1 pH Concentration Change Experiment

Under normal circumstances, in a solution of water, a small fraction of water molecules are dissociated into H⁺ and OH⁻. This is a typical chemical dynamic equilibrium governed by a rate equation for dissociation and recombination. For pure water, the equilibrium concentration of hydrogen and hydroxide is defined to have a pH of 7, where generally pH is defined according to the well-known formula³⁶:

\[ pH = -\log_{10}([H^+]) \]  

(3.2)
The expression in brackets in Equation 3.2 indicates the concentration of hydrogen in moles/liter. For a solution of neutral pH of 7, such as in distilled water, the concentration of hydrogen and hydroxide are both equal to $10^{-7}$ moles/liter.

If $H^+$ were to be removed from a system with neutral pH, the result would be an increase in the pH level of the solution. In a solution of HCl acid, the extra $H^+$ yields a low pH. Consequently, applying a potential difference across two carbon nanofoam electrodes will cause ions to be removed from solution by attracting into the carbon nanofoam and the pH should increase.

To demonstrate this, a solution of HCl in H$_2$O was used with an initial pH of 2.6 +/- 0.2. The uncertainty used was based on the manufacturer’s estimation$^{37}$. In this case the addition of HCl acid in the water greatly increased the concentration of hydrogen in the water, to a level of $H^+$ of $1.5 \cdot 10^{24}$ ions/m$^3$. Two carbon nanofoam electrodes were inserted into the solution and a 10V potential was applied between them. The pH was measured using an Omega PHH-7X digital pH meter and confirmed using Alkacid® pH test paper.

Figure 3.6 shows the experimental setup used for the experiment. This preliminary test was intended simply to check for significant pH changes in the solution rather than to quantitatively analyze them and therefore the experiment was kept relatively simple. A drop of hydrochloric acid was deposited onto a Teflon® substrate. The hydrophobic nature of the Teflon® allowed for a large volume of water to remain on the Teflon® without the need for a sealed container. Carbon nanofoam electrodes were placed in the solution on top of the Teflon®. The total volume of carbon nanofoam used was $6.4 \cdot 10^{-8}$ m$^3$. 0.50ml of HCl acid was deposited, using a syringe, onto the carbon nanofoam. A computer-controlled laser cutter was used to cut the carbon nanofoam into an interdigital pattern described further in Section 5.2.1. Electrical connection to the carbon nanofoam was made by holding NTE electronic 20 gauge copper wire to the nanofoam by hand. A potential of 10V was applied across the interdigital carbon nanofoam for 10 minutes. After 10 minutes, the pH of the solution was measured as 5.4 +/- 0.2, increased from the original value of 2.6 +/- 0.2. After then connecting the carbon nanofoam electrodes to one
another (i.e. shorting out the capacitor) for 10 minutes the pH dropped to 4.0 +/- 0.2. After a further 10 minutes passed with the capacitor shorted, the pH dropped further to 3.6 +/- 0.2.

Figure 3.6: Experimental setup for pH measurements. A cross sectional view, (a), shows 0.5 milliliters of hydrochloric acid on interdigital carbon nanofoam electrodes on Teflon®. In (b), a 10V potential was applied to the carbon nanofoam electrodes.

To evaluate these experimental results, it is straightforward to estimate the expected pH change based upon the experimentally determined capacitance of carbon nanofoam (for NaCl in H₂O), the amount of charge that can be stored for this volume of carbon nanofoam at 10V is (1.7 +/- 0.3) C. The total amount of charge in the volume of HCl acid
used was calculated to be $(1.2 \pm 0.4) \times 10^{-1}$ C based upon the known $\text{H}^+$ concentration. Therefore, all of the $\text{H}^+$ ions should be able to be drawn into the carbon nanofoam.

In comparison, the actual concentration change of hydrogen can be calculated using the measured pH values.

$$\text{Concentration Change} \left[ \frac{\text{moles}}{\text{liter}} \right] = 10^{-pH_1} - 10^{-pH_2} \quad (3.3)$$

$$\text{Relative Change (fraction of initial concentration)} = 10^{(pH_{initial} - pH_{final})} \quad (3.4)$$

The measured pH of the solution changed from $2.6 \pm 0.2$ to $5.4 \pm 0.2$, so the concentration of hydrogen dropped to $(0.16 \pm 0.06)$ % of its initial value. The effect was not reversible, however. The pH of the solution returned to $3.60 \pm 0.2$ instead of the initial $2.6 \pm 0.2$, so the final concentration of hydrogen was only $(10 \pm 4)$ % its original value. This indicates that a substantial amount of HCl remained in or near the carbon nanofoam. This could be a result of adsorption of HCl onto carbon nanofoam or due to a very slow diffusion of HCl ions from the carbon nanofoam back into the solution. Further description of the diffusion processes are described in Sections 5.3 and 5.4.

While this is a preliminary test, it is both interesting and encouraging to find that pH can be significantly controlled using carbon nanofoam as electrodes in an electrolytic capacitor. This may be an interesting opportunity for further research.

### 3.3.2 Dye Concentration Control Experiment

In the next experiment, the concentration of dye in a solution of toluene/methanol was controlled using a similar setup to the one used in the carbon nanofoam capacitance measurements. A photograph of the setup used is shown in Figure 3.6.
Each vial contains 4.0ml of the same solution, which had concentrations of $3.53 \cdot 10^{22}$ molecules/m$^3$ brilliant blue in a solution of 50% methanol/50% toluene by volume. The solution was prepared by first creating a solution of $(7.05 \pm 0.02) \cdot 10^{22}$ molecules/m$^3$ brilliant blue in methanol and then mix with toluene to yield a solution of 50% brilliant blue/methanol and toluene by volume. The vials were sealed using circular pieces of cardboard of dimensions 5.5mm in radius and 2mm thick that were epoxied to the top of the vial using 3M Scotch-Weld DP-100 epoxy. Two thin slits were then cut through the cardboard using an X-ACTO precision knife and carbon nanofoam electrodes were inserted into the vials through these slits. The dimensions of the carbon nanofoam electrodes were 5mm by 4.0cm. The vials 4.5cm tall and had a diameter of 1.4cm.
Figure 3.8: Vials with brilliant blue dye in methanol and toluene. Different potential differences were applied in each figure. (a) Vial with no potential difference applied. (b) Vial with 10V applied across the carbon nanofoam electrodes for six hours. (c) After 10V applied, vial with the carbon nanofoam electrodes electrically connected for six hours.

Using the experimental setup shown in Figure 3.7 a 4V potential difference was applied to the carbon nanofoam electrodes for six hours. The applied potential was then removed and the electrodes were electrically connected to one another for six hours. Photographs of the vials next to a control vial are shown in Figure 3.7. Figure 3.7a shows the initial vial that was equivalent to the control vial next to it. Figure 3.7b shows the vial after 4V had been applied across the electrodes for six hours. The transmission through the vial in this picture was changed significantly. In Figure 3.7c, the electrodes had been electrically connected for six hours and the vial had returned to approximately its original opacity.
3.4 Transmission vs. Time with Applied Voltage – Dye Concentration Measurements

A Calpac 5mW 635nm laser and photometer were added to the setup described in Section 3.3.2 in order to measure the transmittance of light through the vial. The transmission of the 635nm light was measured using a Melles Griot silicon photodetector in a 5.5cm diameter integrating sphere. The measured voltage was amplified using a Melles Griot large dynamic range amplifier, and the photodetector voltage readings were recorded on a computer using a DAQ card and LabView program.

Figure 3.9: Experimental setup for transmission measurements. The setup is similar to that of Figure 3.4 but a magnetic stirrer in conjunction with a small bent paper clip has been added to increase ion mobility.
To increase the speed at which the ions could be capacitively charged, a 2cm length of paper clip was bent into a right angle and placed at the bottom of the vial. The vial was then placed on a Corning magnetic stirrer and the magnet was spun at setting 8 to speed mixing, because without the resulting turbulent flow, the required diffusion distance through still liquid would be large enough to cause prohibitively long diffusion times, especially because diffusion times scale in proportion to the square of the distance\textsuperscript{38}. The experimental setup is shown in Figures 3.9 and 3.10.

Using this setup, a potential difference of 5V was applied between the electrodes for a period of 100 minutes. The solution had an initial concentration of $1.82 \cdot 10^{22}$ molecules/m$^3$ Coomassie brilliant blue dye in 50\% methanol/50\% toluene by volume. Next, the applied potential was removed and the electrodes were electrically connected to one another for a period of 100 minutes. This cycle was repeated several times while the transmission of a 635nm laser light through the bulk solution was recorded by the data.
acquisition system. A graph of the measured intensity of light along with the applied potential and voltage measured across a series resistor is shown in the Figure 3.11.

![Figure 3.11: Brilliant blue concentration experiment transmission measurements. The applied potential difference (green) oscillated between 5V and 0V. The voltage from a resistor in series (red) indicated the current travelling to the nanofoam. The voltage measured from 635nm laser (blue) shows the relative transmission through the vial.](image)

As shown in Figure 3.11, the maximum and minimum transmission of the laser through the solution is increased with each cycle. We have postulated that the mechanism for this increase could be due to absorption. While toluene normally fills the carbon nanofoam adsorption capacity, the applied potential difference across the electric double layer may be making it more energetically favorable for the brilliant blue ions to adsorb.
The expected transmission of light based on the concentration of dye in the solution can be estimated using Beer’s law, which states that the transmission of the light depends exponentially on the concentration of light absorbing particulates in the solution: \[ I = I_o \cdot e^{-\sigma l N} \] (3.5)

Where \( I \) is the transmitted intensity, \( I_o \) is the intensity of the incident light, \( \sigma \) is the absorption cross section in m\(^2\), \( l \) is the distance through the absorbing medium in meters, and \( N \) is the number density of light absorbers in particles/m\(^3\).

The magnitude of charge discharged during the shorting cycles was measured to be:

\[
\begin{array}{|c|}
\hline
\text{Charge discharged through series resistor} \\
(0.028 +/- 0.002) \text{ C} \\
(0.031 +/- 0.002) \text{ C} \\
(0.032 +/- 0.002) \text{ C} \\
(0.032 +/- 0.002) \text{ C} \\
(0.030 +/- 0.002) \text{ C} \\
\hline
\end{array}
\]

Table 3.3: Charge released from carbon nanofoam. Applied potential difference was 5V during the charging phase and 0V during the discharging phase.

Since the volume of the solution in the vial was 4ml, the expected amount of charge in the vial, based on the ionic concentration, was 0.012C, only about 39% of the observed charge storage depicted in Table 3.3. This suggests that the carbon nanofoam was attracting other ions in addition to the brilliant blue dye ions.

The laser light intensity transmitted through the vial increased by as much as a factor of 2000 when a 10V potential difference was applied across the carbon nanofoam.
electrodes. Rearranging Equation 3.5, the concentration change required for the transmission to increase by this factor is:

\[ N = \frac{\ln(I) - \ln(I_0)}{-\sigma l} \]  

(3.6)

where \( N \) is now the change in concentration of the light absorbing species, \( I \) is the measured transmitted intensity, \( I_0 \) is the initial transmitted intensity, \( \sigma \) is the absorption cross section, and \( l \) is the path length through the solution.

The absorption cross section for the Coomassie brilliant blue dye molecules used in this experiment is \( 1.797 \times 10^{-20} \text{ m}^2 \) at 620nm\(^40\), and the path length was twice the inner radius of the vial, or 1.2cm. Based on the measured transmitted intensities, the dye concentration change was \((3.52 +/- 0.5) \times 10^{22} \text{ ions/m}^3 \). From before, the estimated initial concentration in the vial was \((1.82 +/- 0.05) \times 10^{22} \text{ ions/m}^3 \) therefore the numbers are not within uncertainties. It is possible the error lies in the absorption cross section for brilliant blue as reliable data for the absorption cross section for brilliant blue at 635nm was not found.

3.5 Conclusion

In conclusion, the specific volumetric capacitance of the carbon nanofoam material was determined to be \((2.6 +/- 0.3) \times 10^6 \text{ F/m}^3 \) for 6.1 moles/liter NaCl in water and solution of \( 1.76 \times 10^{-3} \text{ moles/liter brilliant blue dye in methanol} \) to be \((1.60 +/- 0.3) \times 10^6 \text{ F/m}^3 \). Charging of a carbon nanofoam electrolytic capacitor was then used in order to change the ionic concentration of the solution. This was demonstrated for a solution of hydrochloric acid, yielding a pH change from an initial pH of \((2.6 +/- 0.2) \) to \((5.4 +/- 0.2) \). After discharging the capacitor, the pH returned to about \((3.6 +/- 0.2) \). The effect was also demonstrated in a solution of dye ions in methanol/toluene, where the concentration change was observed not in a pH modification, but rather as a change of the light transmission through the solution. The transmission of light through a vial of brilliant blue in methanol/toluene was increased by a factor of \((2 +/- 0.2) \times 10^3 \) when a potential difference of 5V was applied to the carbon nanofoam electrodes and then the
transmission returned to approximately its original value when the capacitor was discharged.
4 Transmission Control Devices

The following sections concern an assembly designed to use the ionic concentration control effect presented in the previous section to control the transmission of light in a potentially useful manner. Section 4.1 begins by describing this design, Section 4.2 describes experimental light transmission measurements using this assembly, Section 4.3 analyzes the results, and Section 4.4 considers some of the electrochemical reactions that may be taking place in the assembly.

4.1.1 Description of Device

The time response of the experiments described in the previous chapter were quite slow, with the time required to transition between high and low transmission states (i.e. clear and dark solutions) being of order several hours. The time required to charge the capacitor was dependent on the electrophoretic mobility of the ions and the distance the ions had to travel in order to be capacitively charged to the carbon nanofoam. One objective of the design described here was to reduce this transition time. It was postulated that this reduction could be achieved by substantially reducing the distance the ions were required to travel in switching between the light and dark states.

One of the simplest ways to reduce the ion migration distance involved reducing the separation distance between the two parallel plates of carbon nanofoam as much as possible. This reduced distance no longer provided sufficient space for the laser beam to pass between the electrodes, so in order to observe and change light transmission, two aligned adjacent holes were made in the nanofoam to enable the laser beam transmission measurements.
As shown in Figure 4.1, two circular pieces of carbon nanofoam having a diameter of 8mm were separated by a thin circular ring of Teflon® of thickness 0.3mm. The circular pieces of carbon nanofoam had adjacent aligned 1.0mm diameter holes in their centers to allow a test light beam to pass through.

Machined graphite blocks were used to position and electrically connect to the carbon nanofoam electrodes. The nanofoam was not adhered to the graphite, but electrical contact was made between the nanofoam and graphite by mechanical pressure that was applied by clamping the device between two flat aluminum plates. Viton® o-rings were positioned between the graphite pieces and the aluminum plates ensured an airtight seal that contained the electrolyte for the duration of the experiment.
The o-ring groove dimensions were selected such that the applied pressure adequately compressed the o-ring to form a reliable seal. The dimensions for an o-ring groove for a specific type of o-ring are well defined and readily available in many machining manuals. The thickness used for all o-rings was 1.780mm. The recommended o-ring groove depth for o-rings of this thickness is 1.45mm\(^4\). The top and bottom o-ring grooves were machined to this depth, however the center o-ring groove was machined to be 1.142mm such that an airtight seal between the graphite and o-ring could be created while still maintaining a 0.308mm gap between the two graphite pieces. A circular depression was machined into the bottom piece of graphite, to accept and localize the carbon nanofoam, with room for a Teflon\textsuperscript{®} spacer as well. The two graphite pieces and the aluminum clamping plates had holes drilled through their centers to enable a laser beam to be passed through it. These holes were subsequently plugged by a short segment of clear glass rod in order to reduce the volume of ionic solution contained in the device. Two additional o-rings and glass cover plates were used to create an airtight seal around the holes in the graphite. The glass plates on the top and bottom of the graphite pieces also prevented the graphite from coming into electrical contact with the aluminum plates.

The thickness of the carbon nanofoam was 160µm so the total thickness of the two carbon nanofoam electrodes with the Teflon\textsuperscript{®} separator ring was 620µm. The central circular depression was machined to be 300µm deep such that the thickness of the nanofoam and Teflon\textsuperscript{®} ring extended above the top surface of the bottom graphite piece by 320µm. This was designed to ensure that when the stack was clamped, the o-ring would be compressed appropriately and the graphite would make good electrical contact with the nanofoam. Additional Teflon\textsuperscript{®} rings were sometimes placed in-between the graphite plates as an extra precaution to prevent shorting but they were not strictly necessary.

4.1.2 Description of Materials Used

The selection of materials used in the device in Figure 4.1 was complicated by two factors. First, as a result of the need to avoid the adsorption effect in the device, as
described in Section 3.2, toluene was required, but toluene is incompatible with many materials, particularly plastics and elastomers. Second, in order to reduce electrochemical reactions, chemically inert materials were required. A more thorough discussion of the electrochemical processes taking place in the solution is presented in Section 4.4.

The most significant constraint in terms of the materials selection was the presence of toluene. It was found through literature search that toluene dissolves most plastics, many rubbers, and nearly all adhesives. For this reason the carbon nanofoam could not be adhered easily to the graphite. Materials that were found to be compatible with toluene included carbon, Teflon®, and Viton® rubber, so electrical contact between the carbon nanofoam and the graphite was achieved by means of contact pressure between the graphite plates and nanofoam, supported by the Teflon® ring and sealed using Viton® o-rings.

In order to minimize the amount of electrochemical reactions in the device, it was necessary to use chemically inert materials. Since carbon was already being used as an electrode in the form of carbon nanofoam, it was decided that the best possible electrical contacts would also be carbon. For this reason graphite was chosen. Unfortunately, due to the porosity of the graphite, the electrolyte solution soaked into and quickly evaporated through the exposed graphite surfaces. To prevent this, the graphite was filled with EM-400 purified paraffin wax obtained from Leica Microsystems. The wax treatment was accomplished by melting the wax in an oven at 60⁰ Celsius, just above its melting temperature of 56.5⁰ C, and then submerging the graphite blocks in the wax. The graphite block was then left under a partial vacuum of 0.03 atm until no visible air bubbles were seen emanating from the graphite. This took approximately four hours. The graphite piece in the wax was then once more exposed to a partial vacuum of 0.03 atm and pressurized back to 1 atm to ensure that any trapped air had been removed. Finally the graphite was taken out of the liquid wax and was suspended by a string in air until it cooled and the wax hardened. Cotton swabs were used to remove any surface paraffin wax to expose the graphite in the central region so that the carbon nanofoam would be able to make electrical contact. Over the course of several experiments with the graphite,
the paraffin wax treatment was found to degrade over time so the treatment was occasionally repeated to ensure the graphite was adequately sealed by the wax.

4.1.3 Process for Filling Assembly

The device was designed such that it could be carefully filled with the electrolyte. The device components involved and the order of their assembly is displayed in Figure 4.2. First, the bottom aluminum plate was placed on a table with the clamping bolts pointing upwards (1). A square piece of glass with sides 2cm in length was placed properly on top of the bottom aluminum plate, covering the central hole in the aluminum plate (2). The first small o-ring was then placed on the glass (3) along with a glass rod (4). The first graphite piece was placed on these pieces such that the o-ring was put into the groove on the bottom of the graphite piece and the glass rod entered the central hole in the graphite (5). The central o-ring was then placed on top of this graphite piece in the o-ring groove (6). The first circular piece of nanofoam was then placed in the center circular depression (7). The Teflon® separator ring (8) and second circular nanofoam piece (9) were then placed on top. In order for the assembly to be filled with solution, a fluid entry port was required. A long thin piece of Teflon® of dimensions 50mm by 5mm by 0.5mm thick was placed between the central o-ring and a graphite piece (10) to ensure the central o-ring did not create an airtight seal during the filling process. The second graphite piece was then placed on top of this ensemble (11) and the top glass rod was put into the hole of this graphite piece (12). The top o-ring was put into the top o-ring groove (13) and a glass piece was placed onto this o-ring (14). The final aluminum plate was then placed onto this graphite piece (15) and the nuts were screwed onto the clamping bolts (16).
Figure 4.2: Assembly order for transmissive cell.

The apparatus was then submerged in a dye solution of methylene blue in 50% methanol/50% toluene by volume and placed in a vacuum chamber. The chamber was then evacuated to a pressure of 0.03 atm and pressurized back to 1 atm twice. This ensured that the air originally present in the nanofoam and the central space was replaced by electrolyte, along the fluid exchange path created by the Teflon® spacing strip (10). Once the device was filled with electrolyte, the Teflon® strip (10) was removed while the apparatus was still submerged in solution. The aluminum plates were then clamped down and screwed into position to ensure an airtight seal. The assembly was then removed from the solution and the dye solution was cleaned off the exterior.
4.2 Transmission over Time with Applied Potential – Time Response Measurements

Using the system described in the previous section, electrical potential differences were applied between the graphite pieces and the resulting transmission was measured by directing a laser beam through the center of the apparatus, as shown by the setup in Figure 4.3.

![Experimental setup used for transmissive display. A 635nm laser beam transmitting through the display was measured using an integrating sphere and photodetector. A 10cm focal length converging lens was used to focus the laser beam.](image.png)

The cell was filled with an electrolyte having $5.65 \cdot 10^{23}$ ions/m$^3$ methylene blue in a 50% methanol/50% toluene by volume solution. Methylene blue dye was chosen for these experiments because data on its light absorption cross section was more readily available.
in literature than for brilliant blue dye. The transmission of a Calpac 5mW 635nm laser was then measured using a Melles Griot silicon photodetector in a 5.5cm diameter integrating sphere while the applied potential difference was cycled between 5V, 0V, and -5V. For these measurements, both signs of potential were applied across the electrodes to ensure that there was no build-up of charge on either of the nanofoam electrodes and also to confirm that the optical response was independent of the sign of the applied potential, as expected. A 10cm focal length converging lens was used to focus the laser beam through the 2mm diameter holes in the transmissive cell. The integrating sphere, transmissive cell, lens, and laser were positioned on Edmond Optics simple optical mounts approximately 12cm from the table. The transmissive cell and laser were held using two English bar-type holders while the lens was held with an Edmond Optics simple lens holder.

The voltages measured with the photodetector were amplified using a Melles Griot large dynamic range amplifier. These voltages were recorded on a computer using a DAQ card and LabView program. The transmission was first measured for a clear solution (no methylene blue present) and this transmission value was defined as 100%. The subsequent measurements with methylene blue present were normalized to this maximum transmission. The % transmission of light through the cell in response to the applied voltage profile (also plotted), are shown in Figure 4.4. The measurements were actually done over a period of 4.5 hours however only the first 80 minute portion is depicted in Figure 4.4.
Figure 4.4: Transmission measurements for transmissive display. Using the setup in Figure 4.3, the transmitted intensity of a laser through the device was measured. The potential applied to the carbon nanofoam is shown in red and corresponds to the right axis. Percent transmission (blue) corresponds to the left axis and is relative to a display with no methylene blue.

In Figure 4.4, the axis on the right is the potential applied to the carbon nanofoam electrodes (note that although the scaling of the axes are the same, this has no significance because the units of the two axes are different).

The path length of the light through the ionic liquid was estimated to be $8.0 \cdot 10^{-4}$ m based on the thickness of the carbon nanofoam pieces plus the Teflon® separator ring. Using Equation 3.5 and the absorption cross section of methylene blue dye at 635 nm of $1.726 \cdot 10^{-20}$ m$^2$, the expected initial transmission was estimated to be $(0.041 \pm 0.005)$%. The transmission of the light through the initial concentration of solution was
experimentally observed to be \((0.24 \pm 0.02)\%\). It is possible that some laser light was reflecting off another surface and into the integrating sphere, which could explain the discrepancy. The maximum light transmission reached 14\%. Using Equation 3.6, this transmission means the ionic concentration in the device dropped to \(1.42 \cdot 10^{23}\) molecules/m\(^3\), about 25\% of the initial concentration.

To estimate the total amount of charged contained in the device, an electrolyte volume estimate was required. The estimated volume of dye in the device was estimated as the sum of two cylinders. The first was the cylinder with diameter equal to the diameter of the central o-ring with thickness of \(3.1 \cdot 10^{-4}\) m. The second was the diameter of the center circular groove, 10mm with thickness 300\(\mu\)m. This lead to a volume estimate of \(1.52 \cdot 10^{-7}\) m\(^3\). To estimate the volume that could be occupied by solution, 60\% of the volume of the carbon nanofoam (outer radius 4mm, inner radius 0.5mm), \(9 \cdot 10^{-9}\) m\(^3\), was subtracted out due to the carbon nanofoam having 40\% pore volume. The volume of the Teflon® separator ring, \(7.0 \cdot 10^{-9}\) m\(^3\) was also subtracted. The final estimated volume occupied by the electrolyte solution was \(1.36 \cdot 10^{-7}\) m\(^3\).

The total amount of charge that could theoretically be stored in the carbon nanofoam was then determined by multiplying the volume by the ionic concentration times the charge of each ion. This worked out to a charge of \(1.23 \cdot 10^{-2}\) C. We observed the following amount of charge to be discharged from the carbon nanofoam during the first four shorting cycles. The order corresponds to the order of the shorting cycles shown in Figure 4.4.

Note the sign of the charge values in the Table 4.1 alternate since the applied potential alternates in sign. Once again, the amount charge is somewhat greater than the estimated amount of charge associated with the dye ions. This may be due to impurities in the solution.
<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Charge discharged through series resistor during shorting cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (discharging from 5V)</td>
<td>(-1.9 +/- 0.2)·10^{-2} C</td>
</tr>
<tr>
<td>2 (discharging from -5V)</td>
<td>(1.6 +/- 0.2)·10^{-2} C</td>
</tr>
<tr>
<td>3 (discharging from 5V)</td>
<td>(-1.8 +/- 0.2)·10^{-2} C</td>
</tr>
<tr>
<td>4 (discharging from -5V)</td>
<td>(1.6 +/- 0.2)·10^{-2} C</td>
</tr>
</tbody>
</table>

Table 4.1: Charge released from carbon nanofoam for transmissive display. Applied potential difference was +/- 5V during the charging phase and 0V during the discharging phase. The charges in this table have opposite charge due to the applied potential difference alternating in sign.

4.3 Methylene Blue Mobility

To further analyze the time-varying response of this system, it is helpful to quantify the expected time response of the methylene blue ions. The electrophoretic mobility of an ion in a solution can be estimated using Equation 2.4, and the viscosity of the solution was estimated to be the average viscosity of methanol and toluene. The viscosity of methanol is $5.84 \cdot 10^{-4}$ Pa·s$^45$ and toluene is $5.54 \cdot 10^{-4}$ Pa·s$^46$, averaging $5.69 \cdot 10^{-4}$ Pa·s. The relative permittivity of methanol is 32.6$^31$ and 2.40 for toluene. The relative permittivity used was the average of these, 17.5. From Equation 2.4, the estimated electrophoretic mobility of the methylene blue ions in methanol/toluene is thus $(6.80 +/- 0.07) \cdot 10^{-9}$ C·s/kg.

The estimated path length that the ions travel when the cell is charged was estimated to be half the Teflon® separator ring thickness, $1.50 \cdot 10^{-4}$ m, plus half the carbon nanofoam thickness, $1.25 \cdot 10^{-4}$ m, for a total path length of $2.8 \cdot 10^{-4}$ m. Using this estimated path length, one can calculate the amount of time it should take for a methylene blue ion to be attracted into the carbon nanofoam for a given applied potential difference, using the expected velocity of the particle from Equation 2.5 and dividing this by the estimated path length. The initial electric field in the bulk solution is equal to the applied potential difference.
difference, 5V, divided by the separation between the nanofoam electrodes, $3.0 \times 10^{-4}$ m. This gives an electric field of $1.67 \times 10^4$ N/C. The expected speed of the particles when 5V is applied is therefore $1.14 \times 10^{-4}$ m/s. Dividing this number by the estimated path length gives an expected transition time of 0.41s.

However, the method described above is only a rough approximation. A complication arises when one estimates the electric field in the electrolyte. Initially the field can be thought to be a constant, equal to the applied potential divided by the electrode separation. As the cell charges, however, the potential drop across the Debye layer next to the electrode increases and the electric field in the bulk of the solution drops. When fully charged, the electric field in the bulk solution is zero.

The time-varying response of the display is further complicated by the distribution of pore sizes in the carbon nanofoam. In order for the inner portions of the carbon nanofoam to contribute to the capacitance, methylene blue ions must travel a tortuous path. The result is an increasing effective path length for the ions that increases as the carbon nanofoam capacitor charges. Electrically this overall system can be modeled as a series of capacitors in parallel separated by a resistor.
Figure 4.5: Electrical schematic of carbon nanofoam capacitance, showing a portion of the device. The capacitors in the diagram above represent the capacitances of the different pore sizes in the carbon nanofoam. From top to bottom they represent the smallest pores to the largest pores. The resistors represent the increasing path length for the ions to get into smaller and smaller pores.

Such an electrical system does not have a single charging time constant, but rather a time constant that increases over time. A system with a time constant that increases linearly over time has been found to have a solution of the following form, known as the DHARA function\(^{47}\),

\[
V(t) = \frac{V_o - A}{(1 + k \cdot c \cdot t)^{1/c}} + A \tag{4.1}
\]

In Equation 4.1, \(V_o\) represents the initial voltage across the series resistor, \(A\) represents some fixed offset voltage, and \(k\) and \(c\) are constants characterizing the time constant growth. In order to find the best fit for the data to the DHARA function, a least squares optimization method was used. Using the Solver function in Excel, the free parameters \((V_o, A, k\) and \(c\)) were adjusted such that the sum of the square difference between the data and the fit at each point was minimized. Figure 4.6 compares the voltage measured across the series resistor to the DHARA prediction that was calculated using the optimized
parameters. For comparison, an exponential function was fit using the same method. The variables fit for the exponential function were the initial voltage and time constant.

\[
V(t) = (0.282) \exp(-t/168) \\
\]

DHARA Fit:
\[
V(t) = (0.906) (1+0.489 \cdot t)^{0.528}
\]

Figure 4.6: Fit for carbon nanofoam series resistor voltage (log scale). The voltage across a resistor in series with the carbon nanofoam is modeled using both an exponential fit and a DHARA fit. The DHARA function fits much more closely; an indication the cell is not a simple resistor-capacitance circuit.

4.4 Electrochemical Reactions

When electrochemical reactions occur, they change the molecules present and can slowly degrade the electrodes or create gases in the electrolyte. Therefore, it is desirable to minimize the electrochemical reactions in a device in order to maintain the lifetime of the device. To minimize electrochemical reactions, two things are needed: a good electrical...
connection between the carbon nanofoam and the conductor used as well as a conductor that does not easily react with the electrolyte.

Under a strong enough electric field, any molecule will undergo a chemical change. Even in the case of hydrogen, a strong applied electric field will cause the protons to be separated from the electrons. When a strong electric field is applied between two different bulk materials, the materials may undergo a chemical reaction at the places where they are in close proximity to one another. To minimize these reactions, the electric field between these materials needs to be as small as possible. In the device described in this section, there must be an electrically conductive material that connects the carbon nanofoam to an external voltage source. The potential difference between the conductive material and the carbon nanofoam is determined by the resistance of the electrical connection between them. To reduce the potential difference and consequently the electric field, a strong applied pressure was used so the resistance between the materials was low.

In addition, as a secondary safeguard to prevent electrochemical reactions, graphite was used as the electrode. Graphite and carbon nanofoam are both made of carbon, a material which is known to be fairly chemically inert, and therefore these components do not readily undergo electrochemical reactions. However, when the nanofoam is capacitively charged, the majority of the potential drop occurs across the outer Helmholtz plane next to the nanofoam, and the potential drop can inevitably result in a small amount of electrochemical reactions. Using carbon to electrically connect to the nanofoam ensures that even if there is a small potential drop across this connection, there would not be a significant increase in the electrochemical reaction rate caused by dissimilar materials at the interface. If a different material were used that reacted more easily with the electrolyte, it would be possible for the electrochemical reaction rate to be increased significantly in the cell. It was for these reasons that graphite was chosen for the electrodes and, in addition to avoiding chemical degradation from toluene, pressure between the carbon nanofoam and graphite were used for the electrical connection.
4.5 Conclusions

These experiments demonstrated that the transmission of light through an ionic dye solution can be increased by drawing the dye ions out of the electrolyte and into carbon nanofoam electrodes. The original low transmission state can be restored by removing the applied potential and expelling the dye ions from the electrode such that they are redistributed in the electrolyte. Under an applied voltage of 5V, significant transmission changes were observed, ranging 1% to 15%. Based on the transmission measurements, it was estimated that 75% of the dye in the solution was drawn into the electrodes. It was also shown that the time response of the device was not a simple resistor-capacitor dynamic response, but rather it had a time constant that increased when the carbon nanofoam charged. The time response of the device was primarily dependent on the electrophoretic mobility of the ions in the electrolyte and could potentially be reduced by making a thinner device, which would reduce the average distance over which the ions would have to migrate. Such a system could be used to create a transmissive information display that employs a backlight, as is currently the case with most liquid crystal displays.
5 A Reflective System

Transmissive displays are useful in many applications, but low-power electronic paper displays must make efficient use of ambient light, and therefore in these applications reflective displays are preferred. This section presents a design for a reflective display device that could be used for an electronic paper display employing electrical control of dye concentration.

Paper has high reflectance due to the low absorption of the material as well as the many intrinsic optical deflections that occur when light reflects from the cellulose fibers that comprise the paper. It is worth noting that the reflectance of a single cellulose fiber in air is typically only a few percent but nevertheless a high overall reflectance is achieved because of the many reflections that occur.

To recreate the reflective properties of paper, a highly porous non-absorbing material was selected because it maintains a high reflectance, even when submerged in a solution of methanol/toluene. Specifically, we used 250µm thick unlaminated Teflon® membrane filters from Sterlitech Corporation with 1µm size pores. The ionic concentration in the Teflon® membrane was controlled using interdigital electrodes placed adjacent to this membrane (see Figure 3.1).

When ink is printed on paper, it has low reflectance due to the ink wetting the fibers of the paper and absorbing the light that passes through it. To recreate this effect, the Teflon® filter used was placed in a solution of dye ions. The dye ions absorbed light incident on the material creating a dark state. To switch between absorptive and reflective states, a potential difference of 10V was applied between the carbon nanofoam electrodes, adjacent to the diffuser in order to modify the dye concentration in the pores of the diffuse reflector. The reflectance of the diffuser was directly dependent on the dye concentration of the methanol/toluene solution wetting its pores. The following sections describe and present an analysis of the system. Sections 5.1, 5.2, and 5.3 describe the design and how it was assembled. Section 5.4 describes the reflectance changes observed and Section 5.5 analyzes the dynamic response of those reflectance changes.
5.1 Description of Device

In this modulated reflectance device, a highly porous and inert white Teflon® filter was used as the diffuse reflector. In the absorptive state, the filter’s reflectance was greatly reduced by presence of the methylene blue dye ions in methanol/toluene solution that soaked the filter. Dye concentration in the filter region could be electrically controlled by drawing the ions into the interdigital carbon nanofoam electrodes positioned beneath the filter. A diagram of this device is shown in Figure 5.1.

![Figure 5.1: Device schematic for reflective device, side view. Interdigital carbon nanofoam electrodes, in electrical contact with graphite foil beneath the device, are used to electrically draw dye ions into and out of solution. A Teflon® ring is used to apply pressure to create electrical contact. A Teflon® filter is placed in the device to reflect light when the ion concentration is low. Spacer beads are placed between the Teflon® filter and carbon nanofoam to aid in mobility. Viton® o-rings are used for sealing.](image-url)
Figure 5.1 shows a cross-sectional view of the reflective device when it has been filled with a methylene blue in methanol/toluene solution. Light strikes the diffuse reflector, from the top in Figure 5.1, and is reflected or absorbed depending on the dye concentration present in the Teflon® filter. Interdigital carbon nanofoam electrodes were placed under the filter and acted as the electrodes that controlled ionic concentration, and 0.3mm diameter spacer beads were placed in between the filter and nanofoam to allow free movement of the ions (see Section 5.4). A 0.3mm thick graphite foil was placed between the o-ring and Teflon® in order to make electrical contact with the carbon nanofoam. Graphite foil was chosen in this case because it is chemically compatible with toluene, highly conductive, thin, and deformable, which ensured that there was not a large air gap between the edge of the graphite foil, o-ring, and Teflon® base. In addition, graphite foil was used as the electrodes in order to minimize electrochemical reactions as was described in Section 4.4. Carbon nanofoam electrodes were placed into electrical contact with the graphite foil using pressure from a Teflon® ring. Aluminum plates applied the necessary pressure to create an airtight seal between the o-rings and to ensure the carbon nanofoam was put into electrical contact with the carbon nanofoam. A second Teflon® ring was used to keep the o-ring in place. To ensure an airtight seal, aluminum plates were used to apply pressure in a method as was described in Section 4.1.2.

Figure 5.2 shows the same view with a potential applied across the carbon nanofoam electrodes. In the diagram, the light absorbing negative dye ions have been attracted into one electrode while the positive ions have attracted to the other nanofoam electrode. The movement of the ions causes the dye concentration in the region of the white reflective filter to be greatly reduced.
Figure 5.2: Reflective device with potential applied across electrodes. When a potential is applied across the interdigital electrodes, the light absorbing dye ions migrate to one electrode while the counter-ions move to the opposite electrode. The dye concentration in the Teflon® filter drops and the filter no longer absorbs light, but reflects it.

Figure 5.3 shows the same device from a perpendicular viewpoint. The Teflon® filter is only partially shown to display the interdigital carbon nanofoam electrodes underneath.
In this view it is easier to see why the graphite foil needs to be thin and conformable. At the edge of the graphite foil, at the location the foil extends between the Teflon® and the o-ring, there exists a small air gap at the edge, the size of which depends on the thickness of the graphite foil. In order to create an airtight seal, small drops of Loctite Superflex® clear RTV silicone adhesive sealant were applied at the interface between the graphite foil and the o-ring, in order to fill these small holes. In general, silicone is not compatible with toluene, however only very small amounts were required to seal the holes, so this approach provided a sufficiently good seal for the duration of these experiments.
Figure 5.4: Experimental setup for reflective device. The picture is of an aerial view of the device now sandwiched between aluminum plates, which apply pressure to the device. The cell has been filled with methylene blue in methanol/toluene. In (a) no potential has been applied. In (b) a 10V potential has been applied to the electrodes and attracted the ions into the nanofoam.

Figure 5.4 shows the device placed in between two aluminum plates that were clamped and screwed together to apply the pressure required for the o-rings to seal. The view of the device in Figure 5.4 is a top view identical to Figure 5.3, but with the addition of the aluminum plates. On the sides the graphite foil electrodes are shown protruding out of the device. Through the hole in the top aluminum plate, the appearance of the Teflon® filter filled with the methylene blue in methanol/toluene solution is dark blue when no potential has been applied to the electrodes (a), but appears light gray when a 10V potential has been applied to the electrodes (b).
5.2 Fabrication Techniques

The fabrication of the reflective based display involved three main challenges: creating interdigital carbon nanofoam electrodes, assembling the device without the use of adhesives, and filling the device without introducing impurities.

5.2.1 Interdigital Carbon Nanofoam

In order to minimize the characteristic time constant for charging or discharging the device, it was necessary to minimize the path length needed for the ions to travel to the carbon nanofoam (see Section 4.3). An interdigital electrode design, in which the electrode strips are interleaved, achieves this goal.

The fabrication of the very thin interdigital electrodes was difficult to do by hand for small size scales since it was difficult to cut thin strips of the material without breaking them. However, we found that a computer-controlled Versa 50W CO$_2$ laser$^{48}$ could reliably cut the electrode strips from a single piece of carbon nanofoam. This relatively low power laser is typically used to cut wood and plastic, but by using 100% power (50W) and running at 10% of the normal speed, 127µm thick carbon nanofoam could be cut cleanly. 254µm thick carbon nanofoam was not as easily cut under these same settings; the cuts were not always all the way through the carbon nanofoam. The pattern shown in Figure 5.5 was traced out by the laser to create the interdigital carbon nanofoam.
The dark lines shown in Figure 5.5 indicate the laser cutting pattern. The pattern was constructed of rectangular boxes so that the portions of material to be removed could be easily broken off during the cutting process. While cutting, the laser moved in along the lines in Figure 5.5 in such a way that one full rectangle was cut at a time. The laser used pressurized nitrogen to clean off particulates during cutting. Without the rectangular cutting patterns the portion cut out in between the digits was a continuous piece and was
found to bend and move due to the air flow, occasionally blocking the laser or acting as a sail, causing a torque to the carbon nanofoam. With the rectangular pattern the pressurized nitrogen removed the small rectangles of carbon nanofoam as the pattern was cut.

The digit width used in the following experiments was 1mm; however the laser is capable of cutting much finer digits. These finer digit thicknesses were not used in these experiments as it was found to be difficult to keep the digits from touching each other, with caused them to short out. The thickness used was found to be sufficient for this preliminary experiment in order to reduce the path length of the electrodes while still being relatively easy to prevent electrical shorts.

5.2.2 Device Assembly

Adhesives were undesirable in the device as they were quickly dissolved by the toluene in the electrolyte solution. As a result the many pieces of the device needed to be assembled without the aid of adhesives. Although it was possible to carefully place the graphite foil on the Teflon®, followed by the interdigital carbon nanofoam, Teflon® ring, and glass by hand, it was a difficult process that often involved many attempts.

A slightly modified version of the device used carbon nanofoam that had been thermally bonded to the Teflon® base. To create the bond, a 1cm diameter circular section of carbon nanofoam, patterned with an interdigital pattern by a computer-controlled laser, was carefully placed on the center of the Teflon®. A rectangular block of lead, of dimensions 6cm by 6cm by 8cm (weighing approximately 3 kg), was then placed on top of the nanofoam in order to apply pressure between the Teflon® and nanofoam. Next, the Teflon® was heated on a hot plate in a fume hood to approximately 260°C, near the melting temperature of Teflon® of 327°C. The weights were left on for two hours and the Teflon® was cooled back to room temperature. The result was that the softened Teflon® was pushed into the pores of the carbon nanofoam and, when cooled, solidified creating a strong mechanical bond. The advantage with this method was that it avoided
the problem of the interdigital fingers moving into electrical contact with each other during assembly.

With the carbon nanofoam bonded directly to the Teflon®, the graphite foil was placed over the carbon nanofoam followed by the inner Teflon® pressure ring. Finally, the o-ring plus glass and outer o-ring container ring were placed on top of the graphite foil. The Teflon® pressure ring then pushed the graphite foil onto the carbon nanofoam when pressure was applied. The entire device was then clamped between aluminum plates that were connected by fours nuts and bolts to apply pressure.

Finally, in order to fill the device with the methylene blue in methanol/toluene solution, the entire assembly was submerged into the solution, and a similar evacuation filling process as described in Section 4.1.3 was used. A long thin piece of Teflon® of dimensions 5cm by 5mm by 0.5mm thick was placed in between the o-ring and glass in order to allow fluid to flow into the device. The assembly was then exposed to a partial vacuum of 0.03atm and pressurized to air three times. Finally, the Teflon® piece was removed while the assembly was still submerged in solution and the aluminum plates were screwed together to increase the pressure to the device. The device was then removed from the solution, quickly dried, and small drops of Loctite Superflex® clear RTV silicone adhesive sealant were placed in the small gaps on the edges of the graphite foil at the o-ring.

5.2.3 Materials

The materials used for the diffuse reflector and the external electrodes were carefully selected, based on a number of important constraints. The diffuse reflector needed to be compatible with toluene, reflective when wetted with methanol/toluene, and highly porous. The external electrodes needed to be electrochemically inert, compatible with toluene, conductive, thin, and conformable.

Initially ordinary paper was used as the porous diffuse reflector as it had the desired optical properties and was porous. It was found, however, that without undesirable paper
additives such as titanium dioxide the paper was nearly transparent in methanol and toluene. This was due to the similar indices of refraction of cellulose and methanol/toluene.

<table>
<thead>
<tr>
<th></th>
<th>Methanol(^{50})</th>
<th>Toluene(^{50})</th>
<th>Cellulose(^{51})</th>
<th>TiO(_2)(^{50})</th>
<th>Teflon(^{52})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Index of Refraction (at 550nm, 20°C)</td>
<td>1.326</td>
<td>1.494</td>
<td>1.557</td>
<td>2.04</td>
<td>1.365</td>
</tr>
</tbody>
</table>

**Table 5.1: Indices of refraction for relevant materials. Indices of refraction listed are for 550nm light at room temperature.**

One would expect a homogenous, non-porous piece of cellulose or Teflon\(^\text{®}\) to exhibit a reflectance value equal to that of the Fresnel reflection. The Fresnel reflection at normal incidence between two materials of differing indices of refraction can be found using the following equation:

\[
R = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2
\]  

(5.1)

In Equation 5.1, \( R \) is the intensity of light reflected relative to the incident light, \( n_1 \) is the index of refraction of the first medium, and \( n_2 \) is the index of refraction of the medium light is reflecting off of.

To calculate the expected Fresnel reflection from a piece of cellulose or Teflon\(^\text{®}\) in methanol/toluene, the index of refraction for cellulose or Teflon\(^\text{®}\) was used as the first index of refraction while the second index of refraction was estimated as the average index of refraction of methanol and toluene, 1.41. Using Equation 5.1, the Fresnel reflections at normal incidence are shown in Table 5.2.
As shown in Table 5.2, both cellulose and Teflon® should be nearly transparent when immersed in a solution of methanol/toluene. However, if the materials are highly porous and scattering, then there are a large amount of Fresnel reflections that add to give a substantial total reflectance.

The amount of reflectance of a porous diffuser was highly dependent on the porosity and scattering properties of the material. Paper containing additives such as titanium dioxide were found to be reflective however the additives caused the resulting solution to have a complex chemical composition. It was desired to have a simpler chemical system in order to better understand the properties of the device.

The index of refraction of Teflon® shown in Table 5.1 has an even weaker Fresnel reflection than that of cellulose. However, the Teflon® filters obtained for the experiment had pore sizes of 1µm and 40% pore volume. They were found to be have a reflectance greater than 90% at a thickness of 500µm when immersed in a solution of pure methanol/toluene. The filter had a much larger reflectance than that of paper due to a larger number of pores creating a larger number of Fresnel reflections within the filter. In principal, cellulose could have been used if it were made thick enough to result in a similar number of reflections; however Teflon® filter had the necessary reflectance at smaller thicknesses.

### 5.3 Reflectance Changes in Response to Applied Potential Differences

To measure the reflectance of the device in its light and dark states, the device was set up as shown in Figure 5.4 and controlled potential differences were applied between the two
interdigital electrodes. The reflectance of a Calpac 635nm laser was measured using a Melles Griot silicon photodetector in a 5.5cm diameter integrating sphere. A Melles Griot bandpass filter with central transmission wavelength 650nm and 80nm band gap was placed in front of the integrating sphere port to reduce noise. The measured voltages were amplified using a Melles Griot large dynamic range amplifier. Voltages from the photodetector were recorded on a computer using a DAQ card and LabView program. In addition, the response was videotaped as it changed. Section 5.4.1 describes the measured reflectance while Section 5.4.2 shows the captured pictures.

5.3.1 Experimental Reflectance Data

The assembly was set up as shown in Figure 5.4. The laser and measuring system were set up as shown in Figure 5.6.
A 330Ω resistor connected in series with the device was used to monitor the charging and discharging of the device. Light that reflected from the diffusely reflective filter was distributed over a wide range of angles, meaning that only a small fraction of reflected light entered the integrating sphere. To achieve meaningful reliable measurements, the photodetector voltage values measured during experiments with methylene blue solutions were compared to those measured when the device was filled with a control solution of pure methanol/toluene. The reflectance measurements from the integrating sphere over time are shown in Figure 5.7.
Figure 5.7: Reflective device reflection measurements. Applied potential differences (black) of 10V, 0V, and -10V are applied to the carbon nanofoam electrodes. The reflectance (red), relative to a device filled with no dye, is shown in red with scaling shown on the right axis.

One can see from the above reflectance data that the response speed is higher than that of the transmissive display. To further understand the time-varying response of the device, the diffusion rates of the methylene blue ions were measured and analyzed, as described in Section 5.5.

Upon further cycling of the reflectance, the cyclical reflectance is shown to not be completely repeatable. A graph of multiple applied potential cycles is shown in Figure 5.8.
Figure 5.8: Reflectance measurements for reflective device over many cycles. The setup was the same as for Figure 5.7; however the measurements were done over a longer period of time. The minimum and maximum reflectance values increase over time.

Likely, the slowly increasing overall reflectance of the device is caused by a mechanism that gradually reduces the overall ionic concentration of the solution. A likely possibility is that of adsorption. It is possible the adsorption is not being entirely prevented by the toluene or that the applied potential makes it more energetically favorable for the methylene blue ions to be adsorbed to the surface rather than that of toluene. Further study would be required in order to increase the lifetime of the device.
5.3.2 Images Depicting Reflectance Changes

In the following photographs, the cell is shown as it responds to an applied potential difference of 10V over 20 minutes and then discharges back to 0V over an additional 20 minutes.

Figure 5.9: Reflective device pictures cropped to only show Teflon® filter. (a) is the state of the device with no applied potential, in (b) the device has been charging to 10V for 8 minutes, in (c) the device has charged to 10V over 20 minutes, in (d) the device was electrically connected to ground for 8 minutes after having been charged to 10V for 20 minutes, and finally in (e) the device has been electrically connected to ground for 20 minutes.

Figure 5.9 shows the reflectance of the filter over time. Initially no potential was applied (a), then a 10V potential was used to charge the device (b & c), and finally the device was discharged (d & e). In Figure 5.9a, the device is filled with methylene blue in
methanol/toluene. No potential was applied; the dye ions in the filter caused the filter to reflect a dark blue. In Figure 5.9b the device had had a potential difference of 10V applied for 8 minutes. At this time the device was not yet fully charged, the light-absorbing dye ions were still being attracted towards the interdigital nanofoam electrodes at a higher potential. The dye concentration in the filter above these digits was increased because it had attracted dye ions, causing a striped pattern in the filter. In Figure 5.9c, the device was fully charged and was in its most reflective state. The carbon nanofoam electrodes are less evident in the picture as the dye ions had mostly been pulled into the carbon nanofoam. In Figure 5.9d, the device had been discharged for 8 minutes to start the return to the dark state. After 8 minutes the device has not yet fully discharged and, though not as evident as while charging, the dye ions diffusing out of the carbon nanofoam resulted in a striped pattern. In Figure 5.9e, the device had fully discharged and was back to its darkest state.

5.4 Diffusion Measurements

To understand the time response of the reflective device, the rate of diffusion of the dye ions through the carbon nanofoam and the Teflon® filter needed to be determined. The following set of experiments was conducted to determine the diffusion rates for methylene blue across a Teflon® filter and across a sheet of carbon nanofoam.

5.4.1 Diffusion Measurements for Teflon® Filter

The experimental setup for the diffusion measurements is shown in Figure 5.14. The setup was modeled based on a standard setup used for diffusion measurements53.
Figure 5.10: Diffusion measurements experimental setup. Two empty syringes are sealed together using a Teflon® filter. Aluminum plates are used to apply pressure between the syringes and Teflon® filter. Magnet stirrer bars are placed in both syringes atop a piece of Viton® that has been wedged into syringe.

The setup shown in Figure 5.10 shows two syringes with their plungers removed and bonded together by applying pressure between the syringes and a Teflon® filter. The Teflon® filter was used as the medium to create an airtight seal between the syringes, as we believe the pressure applied was enough to close the pores of the filter between the syringes. Inside the syringes, however, there was no pressure on the Teflon® filter and the pore sizes in the filter were assumed to be their normal size.
Initially, both syringes were filled with pure methanol/toluene. Loctite Superflex® clear RTV silicone adhesive sealant was used to seal the ends of the syringes. The volume of the syringes used was 13.4ml. The diameter of the syringes was 1.44cm. Magnets were placed in the syringes and the solution was stirred at a frequency of approximately 10Hz in order to ensure rapid mixing of the dye in each syringe. Two rectangular pieces of Viton® rubber of dimensions 1.5cm by 1cm by 1cm were wedged inside the syringes in order to prevent the magnetic stirrers from touching the bottom silicone seal or the Teflon® filter. To fill the apparatus with electrolyte solution, the entire setup was submerged in a solution of methanol/toluene and repeatedly exposed to a partial vacuum of 0.03atm. The depressurization ensured the Teflon® filter was fully wetted with the solvent and that both syringes were completely filled with the solvent. While the setup was still submerged in the solution, aluminum plates were screwed together to apply enough pressure to create an airtight seal.
Next, a syringe was inserted through the top silicone seal and 1ml of solution was removed. 1ml of a highly concentrated solution of methylene blue in methanol/toluene was then inserted into the top syringe such that the total concentration in the top syringe was $2.82 \times 10^{25}$ ions/m$^3$. The setup was then held atop a Corning magnetic stirrer using a tripod stand and Fisher three-prong clamp, and the magnetic stirrer was operated at setting 8. The transmission of a Calpac 5mW 635nm laser was then measured using a Melles Griot silicon photodetector in a 5.5cm diameter integrating sphere. The laser was held using an English bar-type holder. The integrating sphere and laser were situated on Edmund optics optical stands. Using the measured transmission, the concentration of dye
ions in the bottom syringe was calculated. Based upon the concentration change over time, the diffusion coefficient through the Teflon® filter was calculated.

Rearranging Equation 3.6, one finds that in order for the transmission of the laser light to drop to 1% of its initial transmittance, the concentration in the lower syringe must reach $7.6 \cdot 10^{21}$ molecules/m$^3$. This concentration in the lower syringe means the concentration in the upper syringe will be reduced by this same amount. Since this concentration change is only 0.03% of its initial value, the concentration in the upper syringe is assumed to be constant for simplicity of calculation. For the case of a constant ionic concentration on one side of membrane, one can approximate the diffusion rate through the membrane very simply by assuming a constant concentration gradient. The diffusion rates can then be calculated using a modified version of Equation 2.6. Assuming two large volumes of solutions with different concentrations with ion transfer between them occurring purely due to diffusion through a membrane separating them, the diffusion constant can be calculated using Equation 5.2.

$$D = - \frac{\Delta \text{molecules}}{A \cdot \Delta t} \frac{w}{\Delta n}$$

(5.2)

In Equation 5.2, $D$ is the diffusion constant, $\Delta \text{molecules}$ are the number of molecules that transfer across the membrane, $\Delta t$ is the total time, $A$ is the area of the membrane in contact with the solution, $w$ is the thickness of the membrane, and $\Delta n$ is the concentration difference on either side of the membrane. The time it took for the measured transmission through the bottom solution to drop to 1% of its initial value was measured to be 185 seconds, so this was the value used for $\Delta t$.

Using the thickness of the Teflon® filter, $2.5 \cdot 10^{-4}$ m for $w$, the area of the Teflon® filter in contact with the solution, $(1.63 +/- 0.02) \cdot 10^{-4}$ m for $A$, $\Delta \text{molecules}$ as the concentration calculated above times the volume of the syringe, and the $\Delta n$ as the concentration of the initial solution. The final diffusion coefficients for the Teflon® filter were found to be $(3.0 +/- 0.2) \cdot 10^{-11}$ m$^2$/s.

This diffusion coefficient for methylene blue in methanol is $(7.8 +/- 0.3) \cdot 10^{-10}$ m$^2$/s$^{53}$. The measured value through the Teflon® filter was equivalent to $(3.8 +/- 0.4)$ % of the
diffusion rate of methylene blue in methanol. A likely explanation for the difference between the diffusion rates is that the ions are restricted by the tortuous path they must travel in order to traverse through the filter.

5.4.2 Diffusion Rate for Carbon Nanofoam

To measure the diffusion rate of methylene blue through the carbon nanofoam, a slightly modified process to that described in the previous section was used. Unlike the Teflon® filter, carbon nanofoam does not compress when pressure is applied, thus carbon nanofoam could not be used to seal the two syringes in the way the Teflon filter was. For this reason a Viton® o-ring was added between the syringes to create the airtight seal when pressure was applied. The carbon nanofoam extended out past the o-ring. To prevent solution from wetting into the carbon nanofoam and evaporating through the exposed outer portions, the portions were coated with Loctite Superflex® clear RTV silicone adhesive sealant.

Using the same concentration of methylene blue ions in methanol/toluene as was used in the previous Teflon® filter measurements, the time it took for the transmission of the laser through the bottom syringe to drop to 1% of its initial transmission was once again measured. In the case of carbon nanofoam, the time was less than 1 second. A calculation of the diffusion rate using this number yields a rate several orders of magnitude larger than that of methylene blue in methanol/toluene. Upon inspection of the process it was evident that there were a few macroscopic sized holes in the carbon nanofoam. The holes could be seen visually when the carbon nanofoam was held up to the light; bright pinpoints of light were seen transmitting through that had a very small angle range (on the order of a few degrees), indicating the transmitted light is travelling directly through the nanofoam. Due to the size of these holes, macroscopic fluid flow was possible through the holes and diffusion through the smaller pores was negligible.

Due to the large distribution of hole sizes in the carbon nanofoam, the diffusion rate in the nanofoam is dependent on the location in the nanofoam in a complicated way. In order to measure the rate at which ions traverse through the carbon nanofoam, it was
necessary to use a more complicated process that took into account the internal structure of the carbon nanofoam. Instead, for the purpose of this set of experiments, it was reasonable to assume that the diffusion rate through carbon nanofoam is equal to the diffusion rate of methylene blue in methanol/toluene, since the pore sizes are comparable.

5.5 Device Timing Predictions

Using these diffusion rates of the dye ions through the carbon nanofoam and Teflon® filter, the device was modeled using a finite difference method. The method essentially involved modeling the assembly as cubic volumetric elements, each having a uniform ionic concentration. The concentrations in each cube were set to initial values at a starting point in time, and the concentration values evolved as time was increased in finite steps. Based on the time that passed between steps, the concentration of a given cubic volume of the device was found by calculating the diffusion currents through its faces, where the diffusion current was determined by the concentration differences between neighboring cubes. The physical device was cylindrically symmetrical with the exception of the interdigital carbon nanofoam electrodes, so it was reasonable to model a cylindrically symmetric system. The device was modeled using a 2-dimensional grid of differing ionic concentrations. The diffusion coefficients for each portion of the grid were determined by the physical material present at that location. The layout of the simulation is shown in Figure 5.12.
Figure 5.12: Diffusion simulation grid system illustrated. The physical device was modeled in 2D with three materials; carbon nanofoam, methanol/toluene, and Teflon® filter. The diffusion coefficients in each grid based on the material present. The initial ionic concentration was set such that all the dye was in the carbon nanofoam electrodes.

Figure 5.11 illustrates the basic scheme behind the simulation. Each box represents a volume element within the device, where each volume element is assigned an ionic concentration and a diffusion coefficient. The ionic concentration was initially set to a predetermined value, and was then calculated one time step at a time to model the diffusion through the volume. The diffusion coefficient for each volume element was defined to be the diffusion coefficient for methylene blue in methanol in the regions where carbon nanofoam or just methanol/toluene were present \( (D_{\text{Methanol}} \& D_{\text{nanofoam}}) \) and the diffusion rate measured for the Teflon® filter \( (D_{\text{Teflon}}) \) in regions occupied by the Teflon® filter. In order to determine the time-varying response of the device, the system was modeled during its discharging process (from its initial highly reflective state slowly changing to its dark state). The initial concentration in the carbon nanofoam was calculated assuming all the dye in the device was in a volume occupied by the carbon nanofoam.
The system was then stepped through time at 0.1s intervals and the concentration in each volume element was calculated using a finite version of the diffusion equation.

\[
\frac{\Delta \text{molecules}}{\Delta t} = -A \cdot D \cdot \frac{\Delta n}{\Delta x}
\]  

(5.3)

In Equation 5.3, \( \Delta \text{molecules} \) is the amount of molecules that transfer to neighboring grids in a time step \( \Delta t \), \( A \) is the area of the surface connecting two grids, \( D \) is the diffusion coefficient of the grid the molecules are moving into, \( \Delta n \) is the difference in concentrations between them, \( \Delta x \) is the spatial grid width.

Finally, based upon the concentration present in the Teflon® filter, the surface reflectance was calculated based upon the absorption of the dye present using Equation 3.5. The final predicted time for the reflectance of the device to drop by 1/e was found to be (520 +/- 2) seconds. From Figure 5.7, the measured time for this reflectance drop was actually (180 +/- 20) seconds. The discrepancy could be due to turbulent flow in the space between the Teflon® filter and carbon nanofoam.

Further, by assuming a diffuse reflector with a diffusion coefficient equivalent to that of methylene blue in methanol/toluene, the time response of the device could be reduced to 45 seconds. If the device were modified to be thinner, for instance 0.5mm, the time response would drop to about 20 seconds.

In principal, with pore sizes large enough to allow for mixing, the time response could be reduced such that the only factor governing the movement of the ions would be the electrophoretic mobility of the ions. In such a case one could expect the time response of the device to depend on the applied potential difference and the thickness of the device.

For the case of a Teflon® filter, large pore sizes that increased the pore would also reduce the overall reflectance as was described in Section 5.3. In principal, the ideal material would be one that had pore sizes large enough to allow turbulent flow but with an index of refraction value significantly higher than that of methanol/toluene so as to remain highly reflective. Possible examples include sintered metallic powders or a high index insulator such as TiO₂.
A modulated reflectance device employing the principal of ionic concentration control was created and demonstrated and it appears that this technique may be suitable for an electronic paper display. While the results are preliminary, the optical properties of the device were similar to those of ink on paper and were shown to be electrically controllable, exhibiting a change in reproducible reflectance from about 40% to 10%. The time-varying response of the device was shown to be primarily governed by the diffusion rate of ions through the Teflon® filter. The diffusion constant of the Teflon® filter was measured to be $(3.0 \pm 0.2) \times 10^{-11}$ m$^2$/s. Using the diffusion constant, the device was modeled using a finite difference method and the time response was found to be approximately twice the experimentally determined amount, which was reasonable, given the approximate nature of this model. The device was then modeled under optimal diffusion conditions and found it could have a time constant of $(20 \pm 1)$ second. This led to the understanding that scaling the pore size to allow for turbulent flow could significantly reduce the time constant of the device.
6 Conclusion

A new technology for creating an electronic paper display was investigated and demonstrated. The device used highly porous carbon nanofoam as the electrodes in an electrolytic capacitor that is capable of drawing dye ions out of solution in order to modulate either the transmittance or reflectance of a surface. The preliminary devices described here were capable of controllably modulating the reflectance or transmittance of a surface, as well as controlling the pH level of an HCl solution.

Carbon nanofoam was first shown to be able to attract ions with a volumetric capacitance equal to \((2.6 +/− 0.3) \cdot 10^6 \text{ F/m}^3\) for 6.1 moles/liter solution of NaCl in water and for a solution of \(1.76 \cdot 10^{-3}\) moles/liter brilliant blue dye in methanol to be \((1.60 +/− 0.3) \cdot 10^6 \text{ F/m}^3\). Taking advantage of this high capacitance, the carbon nanofoam capacitor was used to change the pH of a solution from 2.6 +/− 0.2 to 5.40 +/− 0.2 and then back to 3.6 +/− 0.2. The nanofoam was also shown to control dye concentrations by increasing the optical transmission of a cell by a factor of \((2 +/− 0.2) \cdot 10^3\) and then back to its original value.

Using the demonstrated ionic concentration control effect, a transmission-modulated device was fabricated and tested. Two carbon nanofoam electrodes were used to control the concentration of dye in a solution contained between them and the transmission through this solution of dye was repeatedly modulated from 1\% to 15\%. From the transmission measurements, it was concluded that 75\% of the dye was controllably drawn into and out of solution.

Finally, a reflectance-modulated device was fabricated using a highly reflective porous diffuser. The diffuser's reflectance was repeatedly modulated from 8\% to 40\% by controllably drawing dye ions out of the region surrounding the diffuser and into the highly porous carbon nanofoam electrodes. The reflectance values were analyzed and the time response simulated using a finite element method. The simulation predicted a time response as of 20 +/− 2 seconds for an ideal thin device whose ion mobility was limited by diffusion.
The results from this research indicate that this may be a feasible approach for making a high contrast reflective display. Additional research could be done to further characterize and optimize the time-varying response of the display.
References


Appendix A: Matlab Code used for Diffusion Simulation

% The following code first builds up a 2-dimensional array with dimensions of size by size and labeled initial. The values in this array represent the dye concentration for each volumetric element of the device. An equivalently sized array, labeled diffusion, is made with the values of the diffusion constant for each element in the device. The simulation then moves one step forward in time at a time, from 0 to timefinal, in steps of timeres. The diffusion from neighboring volumetric elements is then calculated. The corners and edges of the array are calculated in separate loops as they have less neighboring cells (2 or 3) than the main body of the simulation.

% initial matrix sets the initial concentrations of the simulation.

format compact

size=5;
initial=[ones(size,1),zeros(size,size-1)];
diffusion=Dfilter*ones(size,size);
diffusion(1,:)=Dfree;
timeres=.1;
timefinal=1;
for t=0:timeres:timefinal,
    % Calculating corners
    i=1;j=1;
    initial(i,j)=(initial(i+1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
    initial(i,j)=(initial(i,j+1)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
    i=size;j=size;
\[
\text{initial}(i,j) = (\text{initial}(i-1,j) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j-1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
i = 1; j = \text{size};
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j+1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\% \text{Calculating Edges (not including corners)}
\]

\[
i = 1;
\]

\[
\text{for } j = 2: \text{size}-1,
\]

\[
\text{initial}(i,j) = (\text{initial}(i+1,j) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j-1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j+1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{end}
\]

\[
i = \text{size};
\]

\[
\text{for } j = 2: \text{size}-1,
\]

\[
\text{initial}(i,j) = (\text{initial}(i-1,j) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j-1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j+1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{end}
\]

\[
j = 1;
\]

\[
\text{for } i = 2: \text{size}-1,
\]

\[
\text{initial}(i,j) = (\text{initial}(i-1,j) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j-1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{initial}(i,j) = (\text{initial}(i,j+1) - \text{initial}(i,j)) \cdot \text{diffusion}(i,j) \cdot \text{timeres} + \text{initial}(i,j);
\]

\[
\text{end}
\]
initial(i,j)=(initial(i-1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i+1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i,j+1)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
end
j=size;
for i=2:size-1,
initial(i,j)=(initial(i-1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i+1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i,j-1)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i,j+1)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
end

%Calculating body not including edges
for i=2:size-1,
for j=2:size-1,
initial(i,j)=(initial(i-1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i+1,j)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i,j-1)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
initial(i,j)=(initial(i,j+1)-initial(i,j))*diffusion(i,j)*timeres+initial(i,j);
end
end
initial