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MEASUREMENT OF A NEW MICRO SUPERCAPACITOR
AND THE CREATION OF ITS DIELECTRIC MEDIUM

by

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A mi padre, que descansé en paz,
y a mi madre, con mucho amor
Ah-so, it all suddenly seems so clear.
Bill, *Kill Bill Vol. 2*
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1. Introduction
In modern society, the storage of electric energy is important; items such as CD players, flashlights, and laptops all use stored electrical energy to run. There are two objects that store electrical energy: batteries through chemical energy requiring Faradaic oxidation and reduction, and capacitors through electrostatic. While batteries, in general, output a greater charge than a capacitor can store, batteries tend to have much shorter recharging-discharging cycle life than capacitors. Super capacitors, or electrochemical capacitors, attempt to increase the storage capacity of capacitors by using a dielectric.

This thesis deals with a new type of electrochemical capacitor made by the MIT Optics Lab and the Electrochemical Engineering Lab. The new electrochemical capacitor is produced in a way analogous to origami shaping. Common, two-dimensional manufacturing processes are used to create a three-dimensional nano-sized electrochemical capacitor. This origami electrochemical capacitor will, in the end, be of a small scale (micro, if not nano) and have a large capacitance once it can be folded multiple times. As of right now, the origami electrochemical capacitor, in its initial state, is not folded into many layers.

This thesis consists of two parts. The first part deals with the creation of an electrolytic solution for the new electrochemical capacitor’s usage. The thesis then attempts to measure the capacitance of the new electrochemical capacitor. To accomplish this however, other capacitors are first measured to make sure the methods and apparatus are appropriate for testing the origami electrochemical capacitor.
2. The Theory of Electrochemical Capacitors

Three parts compose this section of the paper. The first section discusses the solutions and molarity. One section discusses the theory behind electrochemical capacitors; another section discusses the theory behind frequency responses, an important aspect of calculating the capacitance of the capacitor.

2.1 Molarity

To calculate molarity, the following, simple equation must be followed:

\[
M = \frac{\text{# of Moles}}{\text{Volume}}
\]  

(1)

where \(M\) is the molarity and the number of moles is easily calculated using the following equation:

\[
\text{# of Moles} = \frac{m}{\text{atomic mass}}
\]  

(2)

where \(m\) is the mass in grams. Using these equations, one can figure out how many grams of a substance are needed to make a 1M or 0.5M solution. If necessary, the density of the substance can be used to discover how many milliliters of a substance are needed to make the solution. For some of the solutions, normality and not molarity, is used to measure the solutions. This is a simple conversion among acids and bases that depends on the number of hydrogen ions (H\(^+\)) or hydroxide ions (OH\(^-\)) that compose the solution. For example, since one potassium hydroxide molecule (KOH) releases one hydroxide ion in a reaction, it has a normality equivalent to its molarity. On the other hand, each sulfuric acid molecule (H\(_2\)SO\(_4\)) releases two hydrogen ions in a reaction, making its normality twice its molarity.

2.2 The Electrochemical or Super Capacitor

Before continuing, this thesis delves further into the differences between batteries and capacitors. Batteries store energy as potentially available chemical energy requiring Faradaic oxidation and reduction of the reagents. This releases charges that then do work by flowing between two electrodes with different potentials (Conway, 11).
Capacitors, unlike batteries, simply use electrostatics to release charges. Capacitors use negative and positive electric charges on their plates to release their charge; this process is a non-Faradaic process (Conway, 11). A non-Faradaic process consists of a charge accumulation achieved electrostatically by positive and negative charges existing on separate interfaces and separated through space. A Faradaic process stores charge through electron transfers that produce oxidation state changes (Conway, 14). The Faradaic oxidation and reduction is irreversible; chemical interconversions, phase changes, and chemical reactions make this process irreversible, as well as shortening the life cycle of batteries. In capacitors, only an excess and deficiency of charges on the plates are established and released (Conway, 12). Thus, ideally, the capacitor's process is reversible.

Electrochemical capacitors, like battery cells, require two electrodes of opposite charges. The charge storage is electrostatic; at each of the two electrodes, double-layer electron charge separations are established across the electrode interface (Conway, 17). Electrochemical capacitors use a dielectric, or an electrolytic medium, to enhance the charge output of the simple, double-layer capacitor. Ideally, capacitor charge release would be purely electrostatic, reversible, and non-Faradaic. Still, for this ideal behavior to be true, capacitor electrodes need to be ideally polarized. When solution decomposition begins or when Faradaic self-discharge processes occur due to oxidizable or reducible impurities, capacitor electrodes begin to lose their ideal polarity. In the case of electrochemical capacitors, the loss of ideal polarity and direct involvement of Faradaic electrode processes occur when:

1. double-layer-type capacitors are overcharged or discharged, leading to decomposition of the electrolyte;
2. the pseudocapacitative component of the capacitance is charged or discharged;
3. the electrochemical capacitor is self-discharged;
4. the basic Faradaic mechanisms of charging or discharging pseudocapacitors of the oxide type occur [Conway, 33-34].

Those are the four reasons for Faradaic processes occurring within electrochemical capacitors.
There are some basic equations and some basic physics helpful in further evaluating electrochemical capacitors, and capacitors in general. This knowledge of physics can then be used to find the capacitance of electrochemical capacitors. For example, in an interfacial charging process with constant current density $i$, potential difference $\Delta V$, and charge $\Delta q$, we get:

$$C = \frac{\Delta q}{\Delta V}$$  \hspace{1cm} (3)

where $C$ is the capacitance. Knowing that the definition of charge is

$$\Delta q = \int i \cdot dt$$  \hspace{1cm} (4)

we get:

$$C = \frac{i \cdot \Delta t}{\Delta V}$$  \hspace{1cm} (5)

where $\Delta t$ is the time interval. Equation (5) applies if the capacitance is constant with potential. The capacitance, can therefore, be calculated by measuring the relation between $\Delta V$ and $\Delta t$, and taking the reciprocal of their slope, or by measuring the relation between $\Delta q$ and $\Delta V$ and taking their slope. Still, there is a point where non-ideal polarizability picks up, and the $\Delta t$ versus $\Delta V$ graph begins to change non-linearly. This change from linearity to non-linearity occurs when the electrode in no longer ideally polarized, and the current simply passes charge into the interface without any Faradaic processes of transfer of charge across the double layer occurring. This then leads to chemical change at the surface of the electrode (Conway, 53-55). The linear portion of the graph still gives us the ideal capacitance of the electrochemical capacitor. Thus, this is one possible way of measuring the capacitance of electrochemical capacitors.

A second method uses a sequence of potential steps, $\delta V$, to cause the charge, $\delta q$, to flow into the interface at a magnitude determined by $C \cdot \delta V$, where $C$ is the capacitance over the potential range. The $\delta V$ pulse generates a current transient, $i_t$, over a small but finite response time. From this, it can be shown that $\delta q$ is the integral of $i_t$ over the time interval (Conway, 55-56). Thus, the capacitance can be calculated from the $\delta q$ response for the pulse $\delta V$. 
Yet, another measure of capacitance can be made through a linear potential-sweep experiment. The applied potential, which is measured with respect to a reference electrode, is varied linearly with time in a three-electrode cell. One can then obtain time-dependent response current through an oscilloscope. Assuming the sweep rate, \( s \), is constant (\( s = \frac{dV}{dt} \)), the capacitative current, \( i \), is

\[
i = C \left( \frac{dV}{dt} \right) = Cs
\]  

(6)

Thus the capacitance, \( C \), can be calculated through the sweep rate and the measured current (Conway, 56-57).

A fourth experiment depends on the capacitor self-discharging. The electrochemical capacitor is left to self-discharge through a load resistance, \( R \). The time dependence of potential is modeled through the following equation:

\[
V(t) = V_o \exp\left[-\frac{t}{RC}\right]
\]  

(7)

Recording the response, the capacitance can be calculated, remembering that \( RC \) is the time constant (Conway, 57).

The final method, one of the methods used to measure the capacitance of capacitors, is called an AC impedance experiment. This method uses a frequency response analyzer and the knowledge that

\[
Z'' = \frac{1}{j\omega C} = \frac{-j}{\omega C}
\]  

(8)

where \( Z'' \) is the imaginary component of the impedance, \( Z \), where \( \omega \) is the frequency (in radians), and \( j \) is the square root of negative one (Nise, 52). Section 2.3 will develop the equations and theory behind the AC impedance test further. For now, it is just important to note that in a Bode plot of the frequency response of the capacitor leads to the fact that

\[
|Z'| = \log\left(\frac{1}{\omega}\right) + \log\left(\frac{1}{C}\right)
\]  

(9)

where \( |Z''| \) is just the magnitude portion of the bode plot—or alternatively, the real part of equation (8).
Acknowledging that the magnitude of the impedance is a function of the frequency, we can see that the y-intercept of the bode plot magnitude can easily give us the capacitance,

\[ C = 10 \frac{|Z'(\omega=0)|}{2\pi} \]  \hspace{1cm} (10)

where \(|Z''(\omega=0)|\) is just the y-intercept and the \(2\pi\) appears because the frequency in the Bode plot is in hertz, while all the equations assume that the frequency is in radians (Nise, 593-598).

Thus, the frequency response analyzer, and the software it includes, can compute the capacitance by fitting a line on the collected data, calculating the approximate y-intercept, and using equation (10) to calculate the capacitance.

Figure 1: Origami Electrochemical Capacitor under Microscope
The origami electrochemical capacitor is similar to the above-mentioned electrochemical capacitors in that it uses a dielectric, along with electrostatics to improve its capacitance. Unlike other electrochemical capacitors, however, the origami electrochemical capacitor is both small and uses two-dimensional manufacturing processes to create a three-dimensional structure of a capacitor with multiple layers and multiple electrodes. While in this thesis, the tested electrochemical capacitor consisted of only two layers and two electrodes, future versions will be more complicated. Figure 1, above, shows the origami electrochemical capacitor. The square in the center, inside the larger square, holds the electrodes and is 450 micrometers by 450 micrometers. The outer square is 750 micrometers by 750 micrometers. The 450 micrometers by 450 micrometers square contains 784 square pyramids with bases of 3 micrometers by 3 micrometers and a wall angle of 54.74 degrees. These pyramids are used to increase the surface area, and hopefully, the capacitance.

2.3 Frequency Response Analysis

One direct response function that characterizes the pseudocapacitance of an electrode is the alternating current generated in response to an alternating voltage. The imaginary component, \( Z'' \), of the impedance represents this response, and is linked to the capacitance through equation (8) (Conway, 479). Thus, it becomes apparent why this method, called frequency response analysis, is used. This method records the electrical and kinetic response of the electrochemical capacitor over a wide range of frequencies. To record these responses over the range, a phase-sensitive recording device is necessary; usually a frequency response analyzer is recommended.

The data is collected and shown in two different graphical forms, usually on the computer through a program. The first graphical form is the bode plot (absolute value of the magnitude versus the log of the frequency, and the phase-angle versus the log of the frequency). The second graph is the Nyquist plot, which shows the imaginary component of the impedance against the real component of the impedance. For a few, simple circuits, the impedance exhibited at low and high frequencies can be easily distinguished with the following criteria:
1. an ohmic resistance, \( R \), component's impedance is independent of the frequency, \( Z' = R \) and the phase angle is zero throughout
2. a pure capacitor with capacitance \( C \) has a frequency-dependent imaginary impedance \( Z'' = \frac{-j}{\omega C} \) and a phase angle equal to \(-90^\circ\) throughout
3. a pure inductor with inductance \( L \) has a frequency-dependent imaginary impedance \( Z'' = j\omega L \) and a phase angle equal to \( 90^\circ \) throughout (Conway, 482-483).

These basic rules help in deciphering the data collected for the electrochemical capacitor.

Ideally, an electrochemical capacitor would only have capacitance; however, in reality, electrochemical capacitors have ohmic solution resistance, ohmic interparticle contact resistance, and some Faradaic leakage resistance due to overcharge. Electrochemical capacitors, therefore, consist of a complex combination of \( C \) and \( R \) components. For our experimentation, however, the capacitance is probably so much greater than any resistance exhibited in the electrochemical capacitor, that assuming the resistance negligible is acceptable. If this is not true, the results will show components related to those found in resistors.

It is important to understand the principles and concepts behind the evaluation of capacitor impedance; thus, this paper discusses the necessary principles. The experiment uses alternating voltage (AV) to discover the response. The AV in sinusoidal modulation is mathematically described by

\[
V(t) = V_o \sin(\omega t)
\]  

where \( V_o \) is the amplitude of the AV signal and

\[
\omega = 2\pi f
\]

where \( f \) is the frequency in hertz. When \( V(t) \) is applied to a resistor, a current appears. This current is mathematically described by

\[
i = \frac{V(t)}{R} = \frac{V_o}{R} \sin(\omega t)
\]
Using the definition of current as the rate of passage of charge over time, and the definition of charge as the capacitance times the voltage, we get

\[ i = \omega CV_0 \cos(\omega t) \]  

(14)

Thus, if the AV input is a sine function, the corresponding response current is a cosine function. Using the trigonometric rule that \( \cos(x) = \sin(x + \pi/2) \), we see that the current is out of phase with the voltage by -90 degrees.

The equivalent resistance, or impedance, of a capacitor can also be quickly obtained. The definition of impedance is just voltage divided by current. Since from equation (14) we know that \( i_0 \) is simply \( \omega CV_0 \), we get that

\[ \frac{V}{I} = \frac{V_0}{\omega CV_0} = \frac{1}{\omega C} \]  

(15)

Further still, we also know that the current is out of phase with the voltage; thus, we need to add a \(-j\) to equation (15) to get our result. This result, of course, is the same as equation (8). Simple manipulation of known solutions and of the frequency domain has proven equation (8).
3. Analyzing the Capacitors
There are three different methods throughout this experiment; the first involves the creation of electrolyte solutions and testing of these solutions. The other two involve using a frequency response analyzer and potentiostat/galvanostat to measure the behavior of capacitors and the electrochemical capacitor.

3.1 Electrolyte Solutions
The creation of the solutions was straightforward. The first, and most critical step, was the calculation of the needed normality and molarity. Equations (1) and (2) were used to do this. This step was facilitated using Microsoft Excel. The atomic mass, total volume, and if necessary density of the acids and bases were the only things needed to make the solutions.

For the sulfuric acid and hydrochloric acid solutions, a round-bottom flask of either 100 mL or 250 mL (depending on the molarity/normality) was used to first pour the necessary amount of water and then the necessary amount of acid. A standard beaker was used to measure the necessary water and acid. Whenever the amount of acid needed was smaller than could be accurately measured using a beaker, a pipette was used. To measure the necessary mass of base to insert into the flasks, a balance was used. For the acids, the solution was allowed to sit in the flask for a day or two to secure the solution was mixed well. For the base, the solutions was taken out of the glass flasks and placed in plastic containers. This was done to prevent the basic solution from reacting with the glass. The basic solutions sat for a day as well; this made sure the solution was well mixed.

Once made, the solutions were tested to make sure the solutions did not disintegrate or in any other way harm the origami electrochemical capacitor. To do this, scrap origami electrochemical capacitors were placed in the solutions, and allowed to sit in the solutions for up to two days before being checked. These scrap capacitors were then inspected under a microscope. If no damage was visible, then the solution was used with the electrochemical capacitor.

3.2 Frequency Response Analyzer
The testing of the capacitor through the Nyquist criterion and Bode plots used the Solatron 1260 Impedance/Gain-phase
Analyzer connected to a computer to collect the data. The program ZPlot then saved the data and showed the Bode plot and Nyquist diagram for the recorded response. The capacitor was attached to the Solatron 1260 through alligator clips—one for a positive terminal, one for a negative terminal, and one for ground. These alligator clips went into the input jack of the Solatron 1260.

The ZPlot program was opened; the frequency range, and input—in this case the Solatron 1260—were selected on the menu screen. The run test button was pressed, which caused the computer and Solatron 1260 to collect data. A line was then fitted on the magnitude plot; this fit then estimated a capacitance for the test subject, as well as giving the slope of the line. The closer the fitted line's slope was to negative one, the more accurate the estimation of the capacitance was. This process was done for many capacitors, with capacitances ranging from a few picofarads to 4 farads, before the electrochemical capacitor was tested.

3.3 Potentiostat/ Galvanostat

A Princeton Applied Research Potentiostat/ Galvanostat Model 263 A, linked to a computer, collected the data, and sent it to the computer in the potentiostat/ galvanostat experiments. The data was collected and viewed through the programs CorrWare and CorrView. To run this experiment, the CorrWare program was opened, and on the main screen, the 263A Potentiostat/ Galvanostat was picked as the measuring instrument. The next steps included adding the new experiment—in this case a galvanostat experiment—and picking the collecting options for this experiment. In this case, the program collected the charge and voltage of the capacitor while a steady current was applied. The steady current was set to 30 or 20 milliamperes, depending on how accurate the 30 mA data seemed. The data was collected and the charge was plotted against the voltage of this experiment. A line was fitted using CorrView, and, as can be seen from Equation (3), the slope of the line was simply the capacitance of the capacitor. This process was done for capacitors in the farads range.
4. Results of Capacitance Testing
The first subsection of this section discusses the results from the acid and basic solutions. The next subsection discusses the results obtained for the non-origami capacitors from frequency response analysis. The third subsection discusses the results obtained for the non-origami capacitors from the galvanostatic test. The final subsection discusses the estimated capacitance of the origami electrochemical capacitor.

4.1 Damage to the Electrochemical Capacitor

The main problem with using acidic or basic solutions as the dielectric for the electrochemical capacitor is that acidic and basic solutions are corrosive. Still, looking at the capacitors placed in the strongest acidic solution made (2.5 molar sulfuric acid) under a microscope showed no visible damage to the capacitor. The same was true for the capacitors placed in weaker sulfuric acids and weaker hydrochloric acid solutions. In fact, the scrap origami capacitor placed in the 2.5 molar (5.0 normal) sulfuric acid showed no signs of decomposition or damage after two weeks of sitting in the solution.

The origami electrochemical capacitor did show major signs of damage when placed in basic solutions. The 0.5 normal potassium hydroxide (KOH) quickly destroyed the capacitor’s electrode, as did the 0.5 normal sodium hydroxide (NaOH). Due to these results, neither basic solutions were used in testing the capacitor.

4.2 Frequency Response Analysis of Simple Capacitors

The following (Figure 2) is one of the many Bode plots obtained through the ZPlot program for a 150 nanofarad simple capacitor; the first plot is the magnitude plot, the second is the phase plot for the capacitor. The most noticeable thing is that there appears to be noise at the lower frequency range (under 100 Hz). The phase plot shows, however, that for the most part the phase is at -90 degrees and the magnitude plot shows a line with a slope of approximately negative one. In reality, the slope of the line fitted on the linear region of the plot (the region without the noise) is -0.999 and the estimated capacitance was 149 nanofarads. Assuming that the actual capacitance was indeed 150nF, this gives an experimental error of less than one percent. Similar experimental errors resulted for simple capacitors with capacitances of 1.02nF and 10pF.
Figure 3 below shows the Nyquist diagram for the 1.02nF capacitor. While the plot looks chaotic, this is mainly due to the noise at the lower frequency levels. If points only within the linear region of the magnitude plot are considered, the Nyquist diagram become what it should be, a straight line near the y-axis (see Appendix A for more plots and graphs).
Fig. 3: Nyquist Diagram for 1.02nF Capacitor. A straight line is visible before the capacitor hits the low frequency region.

Following the measurement of the regular capacitors, three supercapacitors were measured. Two supercapacitors had capacitances of 2F and the other one had a capacitance of 4F. The results for the 2F and 4F supercapacitors are not as nice or as errorless as the ones for the simple capacitors. The frequency response analyzer and ZPlot routinely gave capacitances roughly one-quarter the actual capacitance of the supercapacitors. For example, one run-through with the frequency response analyzer on the 2.5 volts, 4F supercapacitor gave an estimated capacitance of 1.07F (an error of 73%). Not only did the estimated capacitance come out wrong, but also the Bode plot for these supercapacitors did not behave as capacitor Bode plots. The slope of the line for the above-mentioned supercapacitor, for example, was -0.06. Figure 4, below, shows the Bode plot for the 4F supercapacitor. The phase plot is not at -90 degrees and the slope of the magnitude line is nowhere near -1, as expected. In fact, the phase
hovers sporadically between -90 and -180 degrees for frequencies above 10,000 Hz, but stagnates at zero degrees for frequencies below 1000 Hz. Abnormal behavior is also apparent in the magnitude plot.

A similar, although not as extreme, problem arose when measuring a 30 microfarad (μF) capacitor. The Bode plots and the Nyquist diagram do not appear to be wrong; for example, the slope of the line in the linear region was -0.966. Still, the estimated capacitance is 45 μF, an error of 50%. Figure 5, below, shows the Nyquist diagram for the 30μF capacitor. The Nyquist diagram behaves like a capacitor is expected to behave; the line follows the
y-axis nearly to perfection. The only odd thing is that the data looks too nice; the noise that is apparent in all the other capacitors at low frequency levels is not apparent in the 30μF capacitor. While the Nyquist diagram of the other capacitors appeared linear only for high frequencies; at low frequencies the Nyquist diagram went chaotic for all of the other capacitors. The lack of chaos at low frequencies, along with the inaccurate estimation of capacitance by ZPlot, indicated a problem with this experiment when used to measure capacitors in the microfarads range or higher.
4.3 Measuring the Supercapacitors with a Galvanostat

Since frequency response analysis did not work, the first method of finding the capacitance of a capacitor, as mentioned in section 2.2 was then used. The galvanostat did a much better job measuring the capacitances of the supercapacitors than did the frequency response analyzer. Errors on this experiment ranged from 2.25% to 10.5%, again, assuming that the capacitors' capacitances are indeed 2F and 4F.

Figure 6 shows one of the acquired graphs using CorrView. The graph shows the charge of the capacitor against the voltage while applying a constant current (in this case 30mA). The slope of this line turned out to be 3.91, leading to an error of 2.25%. Similar data were
collected for the 2F capacitor and another 4F capacitor. Thus, the frequency response analyzer can be used if the origami electrochemical capacitor is in the nano, pico, or lower microfarads range and the galvanostat can be used if the origami electrochemical capacitor is in the mid-microfarad or farads range.

4.4 Capacitance of the Origami Electrochemical Capacitor

Four of the six origami electrochemical capacitors tested behaved like resistors; indicating that a short had occurred in the devices, and thus, the devices did not work. Still the two functioning electrochemical capacitors had similar behaviors when placed in 0.1 normal, 0.5 normal, and 1.0 normal hydrochloric acid. Due to the toxicity of sulfuric acid fumes, no testing was done on these capacitors with sulfuric acid solutions.

The two working capacitors both worked, albeit not perfectly, for the 0.1 normal and 0.5 normal hydrochloric solutions; both capacitors had difficulties working at a normality of 1. Figure 7, below, shows the Bode plot for the first origami electrochemical capacitor with a

![Fig. 7: First Capacitor, 0.1 Normal HCl, Fourth Test](image-url)
0.1 normal hydrochloric acid as its dielectric. The most obvious element of the figure is the large amount of noise at frequencies below 1000 hertz. For the frequencies above 1000 hertz, however, the magnitude and phase shift closely follows that of a capacitor. Indeed, for this test on the first capacitor with 0.1 normal hydrochloric acid dielectric, the slope of the magnitude line at frequencies above 1000 Hz is -1.0031. The same appears in all of the other four tests that this capacitor with the 0.1 normal hydrochloric acid underwent; a large amount of noise appears at frequencies below 1000 Hz, but the slope is always near -1, and the estimated capacitance falls between 1pF and 2pF in the linear region. Indeed, the values for capacitances obtained through the five experiments for this capacitor and dielectric are as follow: 1.86pF, 1.75pF, 1.53pF, 1.67pF, and 1.38pF. All of these had slopes close to -1.

Fig. 8: First Capacitor, 0.5 Normal HCl, Second Test
Figure 8, above, shows the same capacitor with 0.5 normal hydrochloric acid as its dielectric. Unlike Figure 7, the graph does not appear to be a capacitor. All four tests ran show the same trend. More importantly, the Nyquist diagram, as well as the phase shift, helps identify a region in which the plots behave like the plots of a capacitor. Using this narrow region (between 10,000 and 100,000 Hz) to find the capacitance, we once again get a slope similar to -1 and results that correlate well with the results obtained for the second capacitor with 0.5 normal hydrochloric acid. This test gave a capacitance of 0.53 microfarads and a slope of -0.94. Similar answers (all between 0.2 and 0.8 microfarads) were obtained in the other tests on the same capacitor. The irregular behavior
of the capacitor, however, at all other frequencies tends to show a problem with the capacitor that explodes when the hydrochloric acid's normality is increased to 1. Figure 9, above, shows the Bode plot for the first capacitor with 1 normal hydrochloric acid as its dielectric. The shape in these Bode plots shows a complex system that does not behave like a capacitor. Testing the capacitor with the galvanostat also did not give any reasonable or coherent reading. The same chaotic behavior appears in the second capacitor when tested with 1.0 normal hydrochloric acid.

The second capacitor appears to have a larger resistance, as its Bode plots look more like a resistance-capacitor circuit (RC circuit) than any of the other capacitors. Figure 10, above, shows that at frequencies above 1000 Hz, the second capacitor with 0.5 normal hydrochloric acid, acts like a capacitor, with a slope of -1.12 and a capacitance of 0.15\(\mu\)F. All four tests show the same behavior; the capacitors act like perfect resistors.

Fig. 10: Second Capacitor, 0.5 Normal HCl, First Test
below 1000 HZ, somewhat like a capacitor at higher frequencies. All tests also seem to back the findings of the first capacitor: capacitance below 1 µF, but above 0.1µF.

The same RC circuit behavior is also apparent of the second capacitor with 0.1 normal hydrochloric acid in its Nyquist diagrams. Figure 11, below, clearly shows this RC behavior. In the region of high frequencies, however, capacitor-like behavior is still apparent, and a slope close to -1 is obtained for all the tests in the capacitor region, as well as capacitances between 1pF and 2pF. The Bode plots corresponding to this Nyquist diagram is similar to the Bode plots obtained for the 0.5 normal hydrochloric acid dielectric.
5. Discussion

The Solatron 1260 Impedance/ Gain-phase Analyzer and ZPlot were unable to accurately test capacitors with capacitances above a couple of microfarads. Although this limitation was unknown going into the experiment, it became obvious after testing the supercapacitors. It forced the development of another measuring technique (the galvanostat test) in case the origami electrochemical capacitor reached capacitances in the dozens of microfarads. It appears that the Solatron 1260 does not have the current ability necessary to make an accurate frequency response analysis of high capacitances. Doing research on the Solatron 1260 showed that many scientists believe the Solatron 1260 to have limited current capabilities. Calling Solatron, we discovered that the maximum capacitance the Solatron 1260 can measure is around 10μF. The Princeton Applied Research Potentiostat/ Galvanostat Model 263 A, on the other hand, is not as limited, since it can go up to 200mA or 1A with the 94 option.

The Princeton Applied Research Potentiostat/ Galvanostat Model 263 A has some limitations of its own. In theory, the galvanostat can record the capacitance no matter how large, but to do this, the constant, applied current must become smaller. This is apparent through equation (5). The capacitance of a capacitor can be approximated as constant. The galvanostat has a limited \( \Delta V/\Delta t \) that it can accomplish; thus, there is a cap to the current that the galvanostat can apply. In addition, the smaller the current, the more noise appears in the collected data.

The data recorded from the origami electrochemical capacitors is both soothing and troubling. The capacitances recorded for the 0.1 normal and 0.5 normal hydrochloric acids match well for both working capacitors tested. Unfortunately, the capacitors do not work as smoothly as expected. One capacitor behaves very much like a resistor and capacitor in series; the resistance in this capacitor is, therefore, too high. Both capacitors seem to have problems when their dielectric solution reached 1.0 normal, and the first capacitor tested could not behave predictably in frequencies lower than 1000 Hz. Still, the results point to the usage of a 0.5 normal hydrochloric acid solution as a dielectric leading to large capacitances if the origami electrochemical capacitor has multiple layers.
6. Conclusion
The acidic solutions do minimal damage to the origami electrochemical capacitor, even when exposed to it for two or more days. Unfortunately, the same is not true for the basic solutions; the basic solutions destroy the origami electrochemical capacitors swiftly. This, of course, limits the number of solutions that can be used as dielectrics in this experiment.

The frequency response analyzer does its job well when the capacitor it needs to test falls below the microfarad range (nano and picofarad range), but it cannot test very well in any range higher than a few microfarads. To measure a capacitor with a capacitance higher than approximately 10μF, a galvanostat must be used. The galvanostat accomplishes the job, albeit with lower accuracy and in a slower process.

The origami electrochemical capacitor's capacitance falls within 1pF and 2pF (closer to 2pF than 1) when its dielectric is 0.1 normal hydrochloric acid, but falls between 0.15μF and 0.80μF when its dielectric is 0.5 normal hydrochloric acid. Still, some odd behavior is clearly visible in the origami electrochemical capacitor. Noise and resistance appears to overshadow the capacitor behavior at lower frequencies, a problem that might cause further troubles in real world applications.

To further the experiment, I would suggest attempting the experiment again when the multi-layer origami electrochemical capacitor is completed. Having more functioning capacitors would also improve the experiment. Looking at the working origami electrochemical capacitors under a microscope, it was apparent that the two electrodes were not parallel to each other. The RC behavior of the second capacitor might be due to a short somewhere in the capacitor, and this should probably be fixed. It is also recommended that the sulfuric acid be tested; this could not be accomplished in this experiment because there was no apparatus to contain the fumes of the sulfuric acid from spreading through the air.
WORKS CITED


APPENDIX A: GRAPHS AND DATA FROM SOLATRON

Fig. A1: Bode Plots for 10pF capacitor

Fig. A2: Nyquist Diagram for 10pF capacitor
Fig. A3: Nyquist Diagram 150pF zoomed in to linear region of magnitude plot; notice that it is a straight line.

Fig. A4: Nyquist Diagram 4F; supercapacitors tend to have this shape.
Fig. A5: Bode Plots 2F; slope not -1

Fig. A6: Corresponding Nyquist Diagram 2F
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<th>Capacitance (Farads)</th>
<th>Estimated Capacitance (Farads)</th>
<th>Fitted Line Slope</th>
<th>Percent Error</th>
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<td>0</td>
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APPENDIX B: GRAPHS FROM GALVANOSTAT

Fig. B1: Charge vs. Voltage 2F Supercapacitor A

Fig. B2: Charge vs. Voltage 2F Supercapacitor B
Test 1
Fig. B3: Test 2 for 2F Supercapacitor B

Fig. B4: Another Test of the 4F Supercapacitor
APPENDIX C: DATA SAMPLES FROM ORIGAMI CAPACITORS

Fig. C1: Non-Functioning Origami Capacitor; Notice that it looks Like a Resistor

Fig. C2: Corresponding Nyquist Diagram
Fig. C3: Bode Plot for First Capacitor, Second Test, 0.1 Normal HCl

Fig. C4: Corresponding Nyquist Diagram; Notice the Region Where it behaves Like a Straight Line
Fig. C5: Corresponding Nyquist Diagram to Second Capacitor, First Test, 1.0 Normal HCl