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Lea Rachel Rogers

University of Arkansas, Fayetteville

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**Developing graphene-based supercapacitors for high
temperature applications**

An Honors Thesis submitted in partial fulfillment of the
requirements for Honors Studies in Biochemistry

By

Rachel Rogers

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Biochemistry

J. William Fulbright College of Arts of Sciences

The University of Arkansas

Acknowledgments

Hulusi Turget

Anish Manoharan

Dr. Ryan Tian

Cale White

The University of Arkansas Honors College

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Abstract

Supercapacitors are ideal tools for energy storage due to their wide range of operation temperatures, long cycle-lives, high power densities of up to 13,000 W/kg, and fast rates of charge-discharge thereby having a high specific capacitance. This research reports synthesis of grapheme-based materials using a modified Hummer's method. Graphene oxide synthesized first and then converted to reduced graphene oxide sheets and graphene-powder, which both increase the ionic conductivity due to sp² bonding and a high surface area. These materials were then constructed into a button-cell supercapacitor for testing. For the first supercapacitors, a porous polypropylene membrane (Celgard) that acted as a separator was placed between the reduced graphene oxide electrode sheets. Propylene carbonate diluted in sodium perchlorate solution was used as an electrolyte. As an attempt, we replaced the Celgard with a graphene oxide-COOH membrane. This acted as a better insulator which thereby allowed the ions to pass through. This supercapacitor produced a stable capacitance of 2.752 F/g even at a current density of 100nA which is better in terms of performance. We also obtained a good energy density (2.75Wh/Kg) a higher power density (7800W/kg).

Introduction

New materials and technologies must be made in order to efficiently harvest energy that will provide a low carbon-footprint and low environmental contamination. A solution to energy saving and energy management could involve the use of

supercapacitors because they can store energy in an electrostatic form rather than a chemical form.(2) With rising industrialization and an increase in population, the use of fossil fuels has increased dramatically.(2) The reserves of fossil fuels are progressively decreasing and the continued use of fossil fuels produces devastating effects, such as pollution that threatens human health and greenhouse gases that are associated with global warming. The global demand for power is 13 trillion watts of power while the current every day need for fuel is 1000 barrels per second. (1) This demand for fuel will keep rising and the need for a different type of energy source is vital. In order to create an energy source with a low carbon-footprint and less environmental contamination, different technologies and materials must be implemented.

One potential technology to replenish the energy supply are supercapacitor-devices that store energy in an electrostatic form. Supercapacitors contain two parallel electrode plates that are separated by a dielectric material.(1-4) They can be charged by applying a potential voltage across the electrodes to make the positive and negative charges migrate toward the surface of the opposite ends of polarity. (2). Once charged, the supercapacitor can be connected to a circuit to act as a voltage source. (10)

Supercapacitors vary from regular capacitors in many ways. In general, they have a higher capacitance, higher energy density, use different dielectric materials, and have a fast charge-discharge rate. (5) Regular capacitors use materials such as ceramic, polymer films, and aluminum oxide while supercapacitors use activated carbon materials. (5) In addition, supercapacitors can store more energy than regular dielectric capacitors.(6-9)

Supercapacitors can charge in less than one minute which makes them, in comparison to rechargeable batteries, a more rapidly and accessible form of energy. (1-2) Another perk about supercapacitors is the wide range of operation temperatures (up to at least 600C). (5 &10) They are already being used in the market for automotive and stationary systems and can provide a 10-40% savings of energy.(1)

In order to advance this renewable energy technology towards becoming lighter in weight and towards higher energy densities, supercapacitors will be constructed out of graphene-based materials in the form of freestanding paper-like membranes.

Graphene(GA) possesses many valuable qualities such as high electron mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), high Young's modulus (1.0 TPa), large surface-area ($2630 \text{ m}^2/\text{g}$), high thermal conductivity ($5,000 \text{ Wm}^{-1}\text{K}^{-1}$), excellent optical transmittance (97.7%), electrical conductivity, and flexibility.(1-5) The effective surface area of GA should depend on the layers present with single layers giving a higher surface area than agglomerated layers and thus gives a higher capacitance. (10) GA is a one atom thick layered 2D structure arranged in a hexagonal or honeycomb pattern with sigma and pi bonds(contribute to delocalized network of electron). (7) This allows for it to have a low weight of $0.77 \text{ }\mu\text{g}$ per 1 square meter of GA sheet. (3) These properties make GA ideal for fabrication of membranes because it is a highly conducting material.(4)

However, GA is a relatively expensive material to try to mass produce products in the renewable energy field. To cut costs, graphene oxide(GO) can be fabricated and then reduced to form reduced GO(rGO). GO contains various oxide groups such as alcohol,

carboxylic, and epoxide groups that disrupt the sp^2 hybridized six member carbon ring structure.(7) In general, the epoxide and alcohol groups are bonded above and below the plane of carbon while the carboxylic acid groups are bound to the edges of GO. (9) The disruption of bonds due to the oxygen groups makes GO an electrically insulating material and it can be produced at relatively low cost from a scalable fabrication process. (4) The Kannappan group illustrated the energy density vs power density of an example GO-based supercapacitor and the possible outcomes in Figure 1. (8) The highest power density obtained by this group was around 13000 W/kg, almost two times of that for the dielectric capacitors.

In this research, the first goal was to synthesize a relatively pure GO product then convert it to the rGO or to other derivatives of GO. One method altered the functional groups on GO to mostly carboxylic acid groups(COOH). This was done to test whether GO or GO-COOH was a better insulating material. Studies have also shown that increasing the oxidation level increases specific capacitance so GO-COOH should work better as an insulator. (9) The next goal was to find a method of manufacturing the supercapacitor. A button cell method was adapted to contain a GO or GO-COOH membrane “sandwiched” in between the rGO powder or GA sheets.

Experimental Methods

Descriptive overview: GA-based membranes were modified chemically, based upon the preliminary data, in order to synthesize high-temperature stable and high-capacitance membranes that were optimal for mass production of new supercapacitors. Specifically

by using an IP-protected recipe, the GO was polymerized in a nanometer scale in order to revamp the electrical insulating properties and ionic conductivity. The GO was altered to rGO from physical means (laser burning), chemical reagents(hydrazine, etc.), or reduced in a furnace with temperatures up to 600C without oxygen. The final product had a specific surface area of around 600m²/g and a tunable electrical conductivity.

Quantification of research

1) Synthesis of GO:

To create GO, a modified Hummer's method from literature was employed. Graphite powder(0.2-0.8g) and NaNO₃ (0.2-0.8g of 98+%) was mixed into 23mL of conc. H₂SO₄ solution under stirring in an ice bath for 15 minutes, which was followed by adding 2-6g of KMnO₄ gradually under stirring for 30-60 min in an ice bath. This solution was transferred into an ice bath at 20-60°C for 90 minutes. The resulting black paste was diluted by 20-100mL of deionized water and then stirred for 5-25 more minutes. This was then mixed with 3-10mL of H₂O₂ and 20-60mL DDI water. The final product was washed liberally with dilute HCl, acetone, and finally DDI water and dried at 40-60°C for 24 hours.

2) Synthesis of GO polymer:

Around 50-500mg of GO was dispersed into 100mL of DDI water, and 0.1-0.5g of a cross linker was poured into a different 100mL flask filled with DDI water. The dispersion of GO was mixed with the cross linked solution, and the resultant mixture was stirred for 5-30min at room temperature and washed again liberally with DDI water.

Then the product was dried at 40-60°C. In this experiment, the cross linker was added to increase the amount of carboxylic acid groups on GO.

3) Characterization of GO and GO polymer:

High resolution scanning electron microscope(SEM) images was taken with a *FEI Nova Nanolab 200 Duo-Beam Workstation* operated with a 15 kV electron beam.

Thereafter, fourier transform infrared spectroscopy was applied on the GO to insure it contained the oxygen-containing functional groups.

4) Preparation and burning of GO-polymer membranes:

GO-polymers were mixed in the DDI water at a concentration of 2.6 mg/mL. Then 50mL of the solution was dried at room temperature for 24 hours on a polystyrene substrate to produce a freestanding membrane around 5cm in diameter. Then the membrane was reduced to GA in a furnace at 600C without oxygen. To reduce GO into GA powder, the furnace was heated to 600C and then the sample was placed inside to exfoliate the sample. To fabricate reduced GA sheets the GO sample was gradually heated in the furnace to 600C.

5) Supercapacitor fabrication and testing:

A button cell was used to create the electric double layer capacitor. Both the GO sheets and powder will be tested as conducting electrodes. A Celgard was used at first to separate the two layers of rGO. In other tests, the GO-COOH was then used in the place of the Celgard as a dielectric material. For all tests a propylene carbonate + sodium perchlorate solution was used as an electrolyte.

6) Technical Performance Tests:

The cycling stability of the capacitor was measured by finding the capacitance of the device after the 10th or 1000th cycle. The drop in capacitance was also compared to the literature values. A graph of self-discharge data vs time was collected.

Results

Once the GO was fabricated, the material was characterized with SEM and FTIR. The results are shown below in Figure 2 and Figure 3. The first three tests were done using a Celgard and (propylene carbonate + sodium perchlorate) as the electrolyte. Each supercapacitor utilized had different amounts or types of GA. Supercapacitor #1 and #2 contain GA powder while supercapacitor #3 contain the GA sheet. The parameters of these supercapacitors are shown below in Figure 4. Each supercapacitor was tested multiple times to see if the capacitance levels were stable. Figure 5 shows the charge-discharge current and capacitance of each run for the three capacitors.

Once capacitance values were obtained, voltage vs time graphs were constructed to show what happened to the charge voltage as the number of cycles increased under a constant current. The results of each supercapacitor are shown below. The supercapacitor #1 underwent 10 cycles with a steady increase of charge voltage. The supercapacitor #2 underwent 10 cycles with a steady charge voltage, and supercapacitor #3 underwent 100 cycles of steady charge voltage. These results are shown in Figures 6-8. The Supercapacitor #3 showed the highest capacitance and survival from 1000 cycles. This demonstrates the stability of the charge/discharge voltage and is shown in Figure 9. For the supercapacitor #3, an energy density vs power density curve was

constructed, and is shown below in Figure 10. The highest power density achieved for these supercapacitors was around 1100W/kg.

The other kind of supercapacitor (supercapacitor #4) was created with rGO sheets as electrodes and GO-COOH as the dielectric material. The electrolyte was propylene carbonate + sodium perchlorate. This sample was run over three times, with different parameters for each run. The parameters are detailed in Figure 11. Supercapacitor 4 contained three spacers inside the button cell in order to keep everything compact. The results are shown in Figure 11 as well. The voltage over time for supercapacitor #4 was stable for the 10 cycles of the test and which is demonstrated in Figure 12. Since the supercapacitor was stable at 10 cycles, the capacitance drop over 1000 cycles was tested, and shown in Figure 13. The overall drop in capacitance over 1000 cycles was 0.1F/g. The largest power density value was achieved at 7800 W/kg and is shown in Figure 14. This was close to that for pure the GA version and much higher than other forms.

Conclusion/Analysis

For the supercapacitor #1, Figure 6 clearly demonstrates an increasing charge voltage as the number of cycles increased under a constant current. This result indicates that there was a slight leakage possibly due to the GA powder possibly having contact points with the other side of GA powder at the edges of the supercapacitor. This would greatly decrease capacitance because there would be less separation of charge.

For the supercapacitor #2 utilizing the Celgard and GA powder, the capacitance increased. The Figure 7 shows that the voltage was steadier and did not increase which

shows that there was almost no leakage. Compared to supercapacitor #1, this supercapacitor used much less GA material (10mg GA powder) and had a higher capacitance than supercapacitor #1 so these results are promising.

For supercapacitor 3 utilizing a Celgard and GA sheet, the capacitance increased once again and used even less material than before (1mg reduced GA sheet). The leakage was still present but down to around 2V. Again this leakage could be due to the rGO sheets coming into contact. This supercapacitor had a stable charge and discharge voltage for up to 1000 cycles. Since this supercapacitor contained the highest capacitance of the supercapacitors using a Celgard, a power density vs energy density curve was constructed. Like most supercapacitors, it had a much higher power density than energy density. For this supercapacitor the power density was approximately 1200 W/kg. Compared to the reference GA supercapacitor which had a power density of 13000W/kg this power density is lower and could be improved.

The best type of supercapacitor was supercapacitor #4 that utilized GO-COOH as the middle insulating layer. The GO-COOH material is a more ion conductive material and less electron conductive material so it gives a slight positive charge to the GO-COOH membrane. This explains why the supercapacitor that used this material as the insulator had better capacitance. There was almost negligible leakage, a stable capacitance, and a much higher power density. This supercapacitor was able to reach the highest power density of 7800W/kg.

However, since other lab results indicated that a higher potential power density might be achieved, our button cell supercapacitor should be improved in the future in

order to achieve an even higher power density. For example, other electrolytes such as sulfuric acid and phosphoric acid could be tested to see if the overall capacitance could be boosted. In addition, ion-conductive materials such as Nafion can be mixed with the GO-COOH to make a hybrid membrane that would most likely have a higher tensile strength and is therefore more durable. Then this membrane can be utilized as an insulating material in a supercapacitor.

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Fig.12 Ragone plot of graphene supercapacitor at various charge-discharge rates.

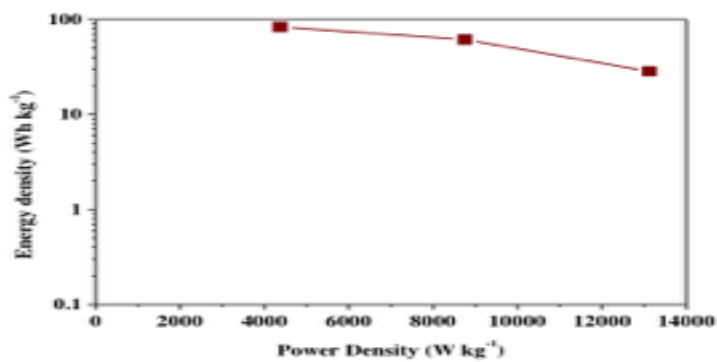


Figure 1: Reference Ragone plot for a graphene supercapacitor

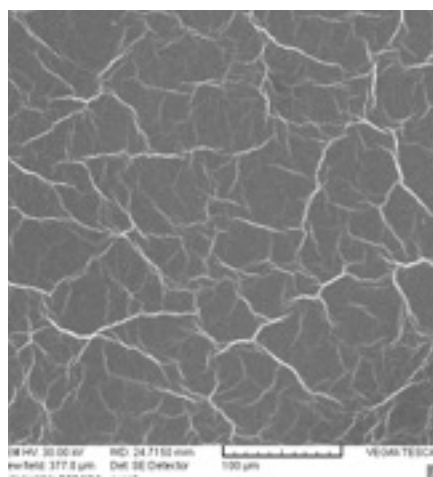


Figure 2: SEM Image of Graphene Oxide

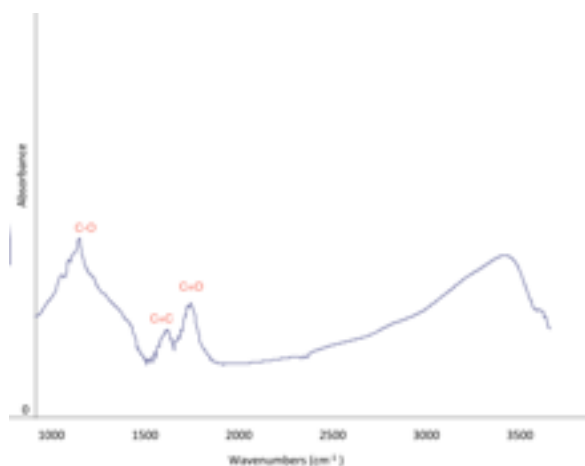


Figure 3: FTIR of Graphene Oxide

Super Cap 1	Graphene powder on both sides Membrane - Celgard Electrolyte - Propylene Carbonate+Sodium perchlorate Spacers - 1+1
Super Cap 2	Graphene powder - ~ 100mg on both sides Membrane - Celgard Electrolyte - Propylene Carbonate+Sodium perchlorate Spacers - 1+2
Super Cap 7	Graphene Sheet - ~0.0009 (1mg) on both sides Membrane - Celgard Electrolyte - Propylene Carbonate+Sodium perchlorate Spacers - 1+2

Figure 4: Parameters of Supercapacitors using a celgard

Sample	Charge current	Time	Discharge current	Time	Cycles	Capacitance
Super Cap 1-1	100uA	15sec	-100uA	15sec	10	0.238 mF/cm ²
Super Cap 1-2	200uA	15sec	-200uA	15sec	10	0.283 mF/cm ²
Super Cap 2-4	500uA	10sec	-500uA	10sec	10	1.375 F/cm ²
Super Cap 2-5	300uA	30sec	-300uA	20sec	10	1.671 F/cm ²
Super Cap 7-1	400uA	30sec	-400uA	30sec	100	2.712 F/cm ²
Super Cap 7-2	800uA	10sec	-800uA	10sec	100	1.777 F/cm ²
Super Cap 7-3	1mA	6sec	-1mA	6sec	100	1.380 F/cm ²

Figure 5: Charge/Discharge times and Capacitance values for Supercapacitors with Celgard

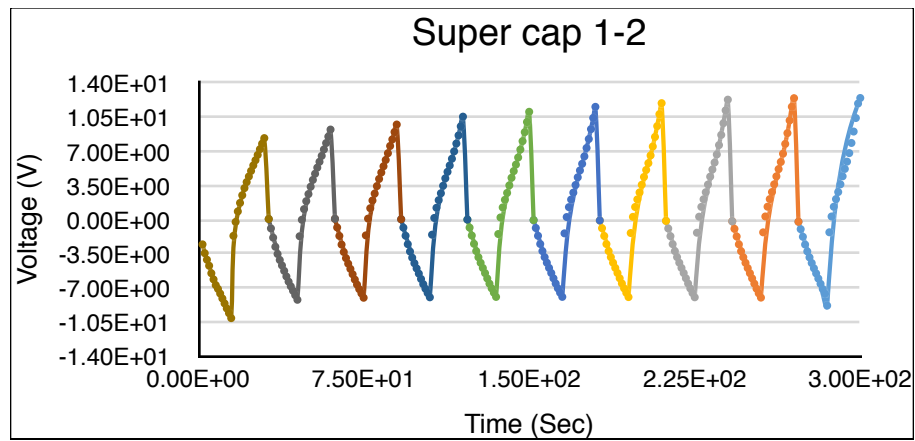


Figure 6: Charge/Discharge voltage for Supercapacitor 1

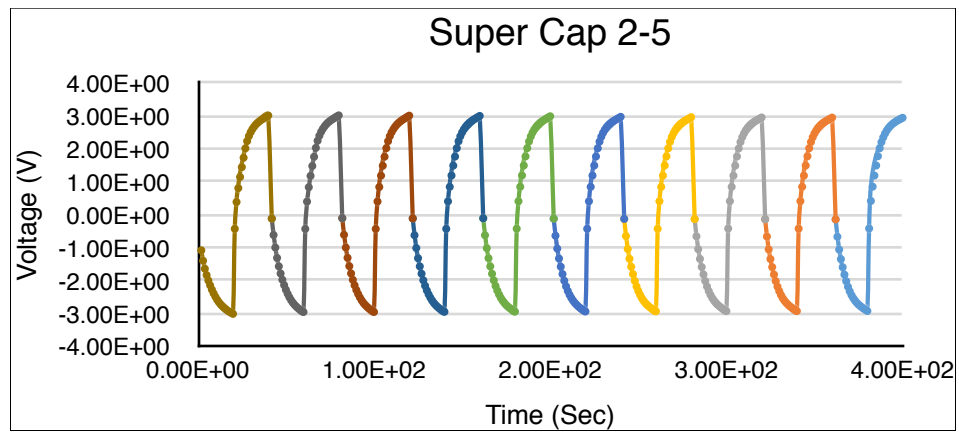


Figure 7: Charge/Discharge voltage of Supercapacitor 2

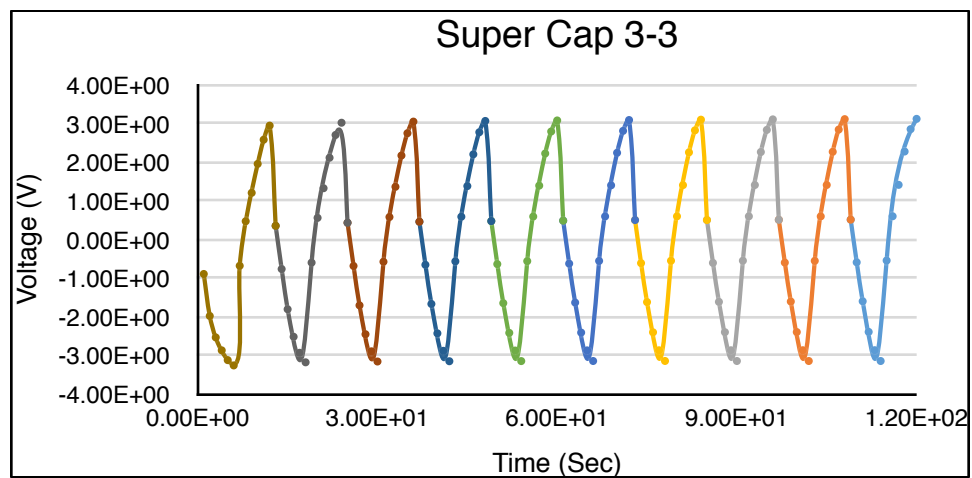


Figure 8: Charge/Discharge voltage of Supercapacitor 3



Figure 9: Charge/Discharge voltage for Supercapacitor 3 (1000 cycles)

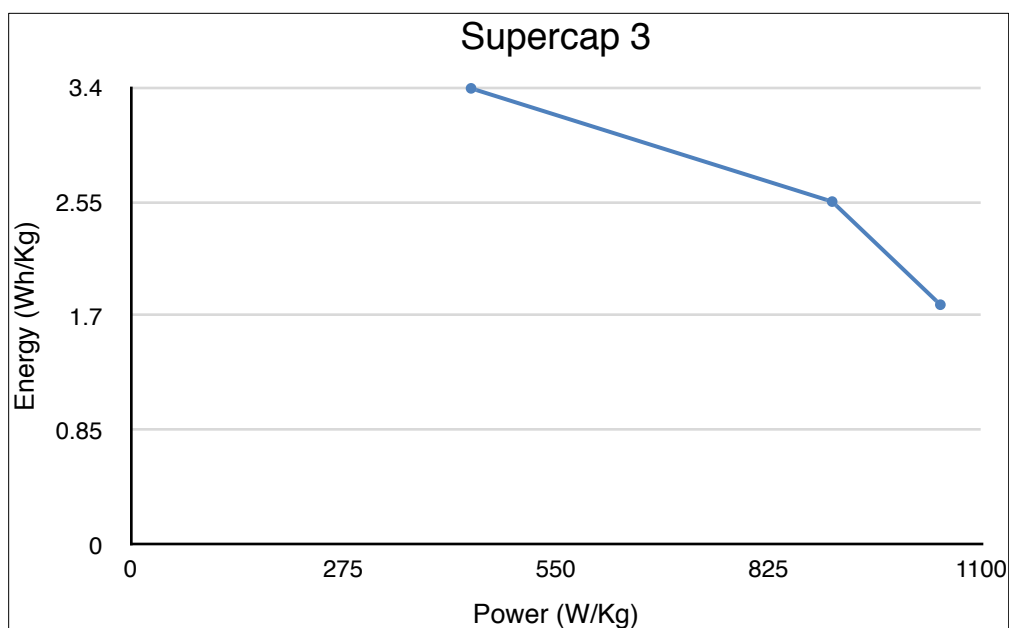


Figure 10: Supercapacitor 3 Energy density vs power density graph

	Charge & Discha	Cycl es	Charging Time period(s)	Discharg e Time Period(s)	Capacita nce (F/g)
Sample 4-1	0.1 A/g	10	60	40	2.752
Sample 4-2	0.2 A/g	10	15	5	1.312
Sample 4-3	0.3 A/g	10	4	2	0.648

Figure 11: Capacitance data for Supercapacitor 4

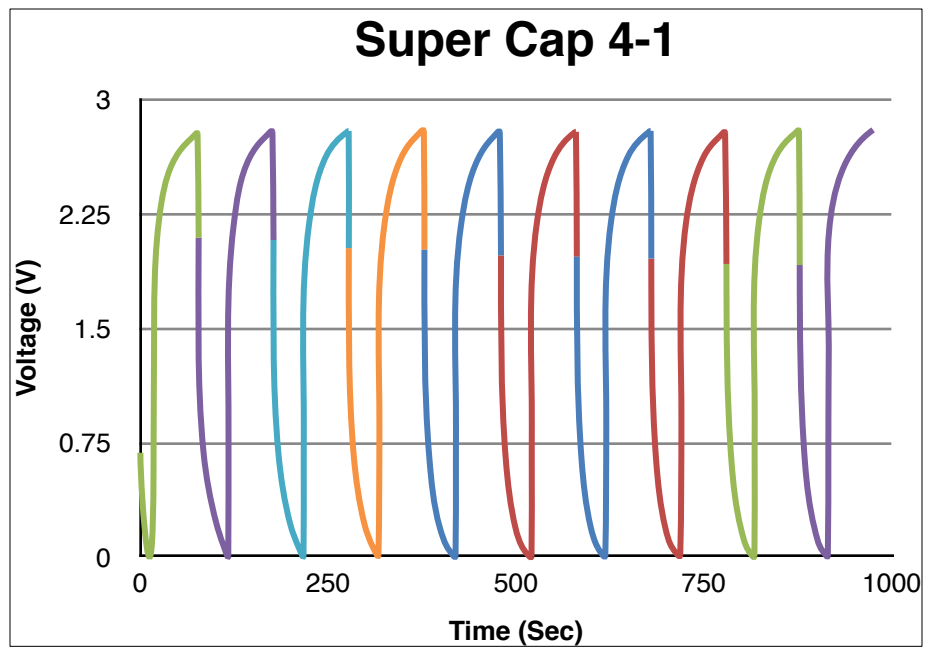


Figure 12: Charge/Discharge voltage data for Supercapacitor 4

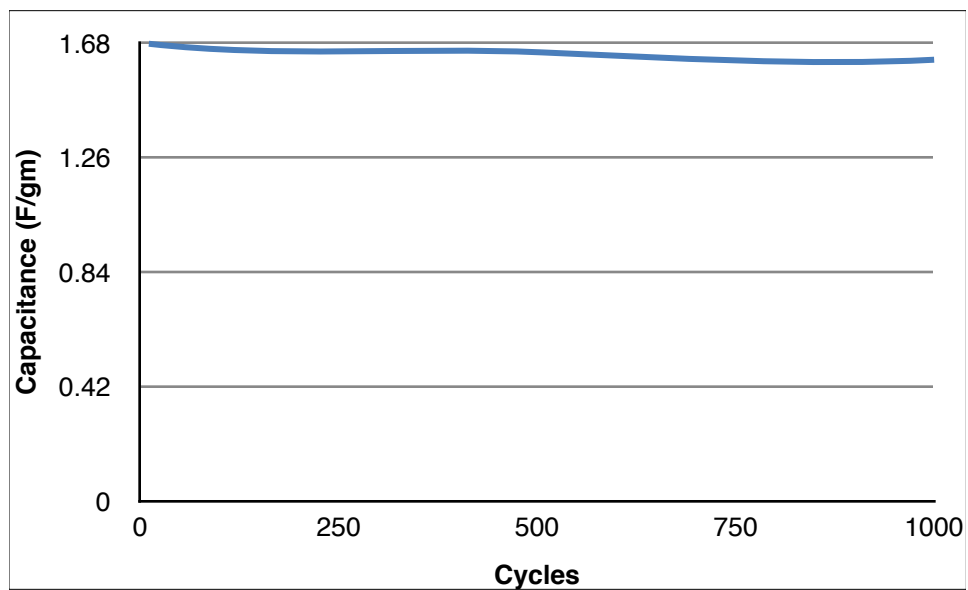


Figure 13: Capacitance vs Cycles graph for Supercapacitor 4 up to 1000 cycles

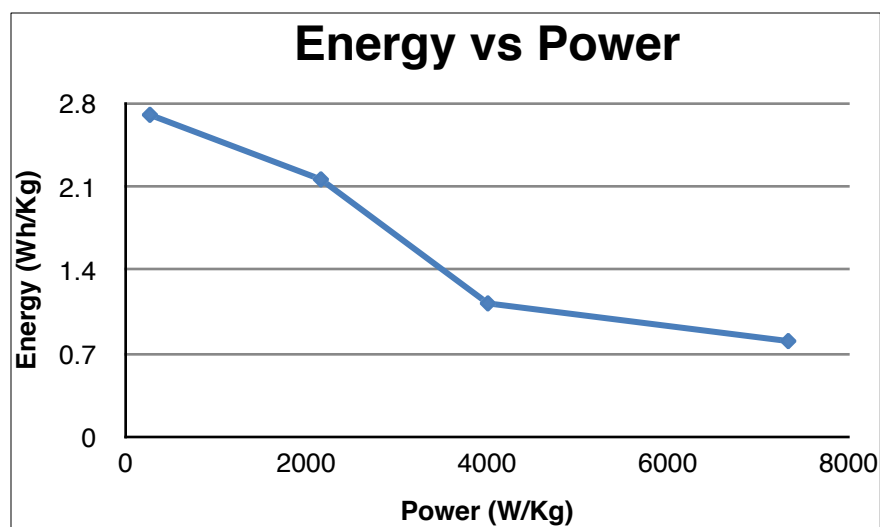


Figure 14: Energy vs Power for Supercapacitor 4