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Fiber-Based Supercapacitor for Wearable Electronics

by

Rohit Lallansingh Yadav

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Electrical Engineering
Department of Electrical Engineering
College of Engineering
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Date of Approval:
July 3, 2021

Keywords: Cyclic Voltammetry, Galvanostatic Charge/Discharge Test,
Electrostatic Impedance Spectroscopy, Specific Capacitance

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Dedication

I wish to dedicate this thesis to my mother, Nirmala Yadav and my father, Lallansingh Yadav who did always support me throughout my master's degree to help me work with the best skills that I got through their continuous motivation. Also, would like to thank my friends and roommates, Sushant and Chaitanya who were always there with me throughout my academic journey and last but not the least my brother and someone special who did start supporting since last one year removing all the obstacles that came my way.

Acknowledgments

First and foremost, I would begin with Dr. Arash Takshi for believing in my potential and providing me an opportunity to work on subject that I was interested in learning. Working with Dr Arash Takshi in these field of engineering part helped me gain a lot and gave a meaning to my Master's degree at University of South Florida. I wanted to thank him for this successful degree completion which could not be possible without his constant knowledgeable lessons, support, help and guidance. I will be forever grateful to him for giving me this opportunity and helping me learn some good skills. I would also like to thank my parents for their support and constant help. I would also like to thank Dr E.K. Stefanakos and Dr Sylvia Thomas for offering me their precious time to serve as the member on my thesis committee. I would also like to thank my uncle, Er. Satish Yadav and my Professor Dr. Shaila Deepak to keep motivating me choose this branch of study. Last but would like to thank the almighty for giving me the hope that I am able to do justice to my project.

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Abstract

Supercapacitors are significant devices that are used for energy storage and also have the capability of delivering energy at a faster rate than batteries. The increase in the significance of portable and wearable electronic equipment giving rise to pace in the development of flexible supercapacitor and flexible electrodes in recent years.

A fiber-based supercapacitor (FSCs) is one of the most significant devices which have even helped us give pace knowing the properties of supercapacitor. These FSCs are said to have excellent electrochemical properties and flexibility. This did make function it in different forms of individual fibers or integrated textiles which make it one of the most promising energy storage devices for wearable and portable electronics.

This thesis discusses about the twisted FSC's which have been studied using three different commercially available conductive threads ad gel type electrolyte. The performance of the device was studied at different number of turns and also lifetime of device was investigated. Furthermore, the feasibility of the sewing machine is also investigated.

The main driving force in developing FSCs is their mechanical flexibility in addition to high capacitive performance. FSCs especially focus on the selection of material, fabrication method its electrochemical, mechanical performance.

The future for FSCs based device trends, prospects, also challenges in terms of its fabrication and assembly.

Chapter 1: Introduction

1.1 Supercapacitors

This thesis even though if it's going through reading on screen or printing on a paper you are utilizing electrical energy. Electrical energy at some point in time is being consumed, stored, even conditioned regardless of any source. Capacitors are used wherever electricity is used, from memory units to small devices such as laptops to large-scale power stations. Capacitors have the ability to store electrical charges based on their capacitance.

The past few decades have shown the continuous change in the global landscape which clearly shows the need for energy which has become the primary focus of the major world powers and the major scientific community. Due to the global need for further use of clean energies, various forms of energy storage devices have been studied extensively in recent years. There are many devices that are related to the storage of energy, one such that device is supercapacitor which has gained a quite good pace in research and development over the last few years and has emerged with the potential to facilitate major advances in the energy storage realm.

The supercapacitor has quite good features in terms of fast charge-discharge rate, high power density, and long operating life. Based on their energy storage mechanisms, supercapacitors are divided into several types: electrochemical double-layer capacitors (EDLCs), pseudo-capacitors, and hybrid-capacitors.

EDLC's store energy by the electrostatic accumulation of charges at electrode-electrolyte interfaces. The properties of EDLC are generally determined by the porosity structure, electrical conductivity, and surface area of the electrodes. Pseudo-capacitors rely on reversible and fast redox reactions for energy storage. Hybrid capacitors are meant to be the combination of EDLC's and pseudo-capacitor electrode and battery electrode in a single electrochemical cell.

Supercapacitors are structurally composed of two electrodes, electrolyte, current collector, and a packaging shell. Electrodes have a very critical impact on the electrochemical performance of the device and thus have been extensively studied. Electrodes are mainly made with materials such as conducting polymers, carbon material (e.g., activated carbon particles, carbon nanotubes, carbon nanofibers, and graphene). While the majority of the device use liquid electrolytes, in recent years, many studies have been conducted on gel electrolytes containing an acid (e.g., H_3PO_4 and HCl).

The flexible electrodes (FEs) and FSCs have not been used yet, but there is a huge potential market for them. In addition, to produce energy, these fiber-like FSCs have a promising future in the field of smart clothing techniques. Using advanced weaving technologies FSCs in different forms and structures can be produced. The fabricated FSCs can be used for developing smart clothes and wearable electronics with desired mechanical characteristics.

1.2 Aim

The main concept and focus for the electrical energy storage device is the combination of high energy density and high power which has been created by evolution from age-old technology to new and advanced technology. Three aims have been accomplished by me in this thesis.

Firstly, it was aimed to study the feasibility of fabricating FSC's by sewing conductive threads and possibility of washing the sample. The FSCs were fabricated using the stitching technique and their specific capacitance has been measured under three different conditions. The first measurement was done on day one of the fabrication (fresh sample), followed by day two. Then the device was tested on the seventh day with the normal testing and later water being sprayed on the device and tested to learn about the effect that it has on the specific capacitance of the device.

Secondly, the effect of twisting fibers for making supercapacitors was studied. The specific capacitance of the fabricated devices was noted on daily basis to analyze their lifetime as well.

Finally, the most important work that is the root of the thesis was to find correlation between the specific capacitance of the devices and number of turns in the twisted structures.

1.3 Scope of Work

The work is on the fiber-based supercapacitor based on a different type of conducting threads being twisted or sewn and doing its analysis on various parameters. The different threads that have been used in making fiber-based supercapacitor are JAMECO (Silver lining-based threads), JL Fiber, and BCP conducting thread thus calculating their specific capacitance from the various testing methods. The tests performed were the cyclic voltammetry (CV) test, electrostatic impedance spectroscopy (EIS), and galvanostatic charge/discharge Test. This thesis mainly focuses on the number of turns made with FSCs and analyzing their specific capacitance.

The next chapter will provide some background information regarding the evolution of capacitors and also the operation of basic supercapacitors. The most two important components for the supercapacitor are the electrolyte (PVA-H3PO4) and the electrode (conducting fiber). Measurements were carried out on different electrodes and getting their specific capacitance. Thus this idea of making fiber-based supercapacitor is been discussed in the chapters.

Chapter 2: Background

The idea of supercapacitors started gaining pace since the 19th century, giving rise to the current technologies to be realizing the renewable, robust in design, and advanced in energy storage that is supposed to be possibly deemed.

The main concept that lies behind supercapacitors (sometimes called ultracapacitors) is having exceptionally high power and energy density and good cycle life. Supercapacitors have a promising operational range between 1 V and 3 V for aqueous electrolytes, which have the potential for rapid charge/discharge and good energy storing capability.

The basic charge storage in supercapacitors relies on the electrical double layer at the interface between electrode and electrolyte. However, it has been quite a bit challenging to create reliable applications for that technology. Supercapacitors have evolved a long way from their basic conception to getting it applied in the upcoming technologies certainly leading its way to prove their application in the older electrical design.

2.1 Capacitor Basics

The basic capacitor comprises two parallel conductive plates separated by the insulating medium (dielectric medium).

Source voltage being applied to the electrodes (terminals) of the capacitors and the opposite charges being developed on the opposite electrode terminal and being charged to a potential equal to the source voltage. When the source is removed, the capacitor maintains the charges on its electrodes. Capacitance is the charge stored in the capacitor is given by equation (1).

$$C = \frac{A\varepsilon}{d} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where C is capacitance, A is the area of the electrode intact, ε is the relative permeability ,and d is the thickness of the dielectric. As the area in contact is increased the capacitance of the capacitor increases, and opposite manner as the thickness of the dielectric medium increases the capacitance decreases and vice versa for both cases.

But, in the case of the supercapacitor the basic knowledge changes. There is no such parallel plate capacitor the electrode can be of any shape size from being a flat plate to a rough plated surface. Specifically, supercapacitors rely on the formation of double layer charges across the electrode-electrolyte interfaces. Because of that, using porous electrodes, extremely large surface areas (i.e., internal surface area of the electrodes) are used for storing the charges. Further details of the supercapacitors can be found in various publications including [1].

A limiting factor is a relationship between charge stored and potential between the electrodes resulting in the energy stored, *E*, in the system is given by equation (2).

$$E = \frac{1}{2} QV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where, *Q* is the charge and *V* is the potential between the electrodes.

2.2 Brief History

Supercapacitors are electrically known as electrical double-layer capacitors (EDLC/ pseudocapacitor). This surface area is meant to be coupled together in double area, giving the device a higher capacitance output.

The first electrochemical capacitor was patented by H.I. Becker (General Electric) in 1957 [25,26,27]. It was quite impractical in the application as the electrodes needed to be immersed in the electrolyte. Today, there is a use of standard EC design that was designed and invented by Robert A. Rightmire but could find use and its application but the design was patented by Nippon Electric Company (NEC). This design was later sold by them named under "supercapacitor" the year 1975 [26].

Later, many other industries went on to design their own ECs after the commercialization of design by NEC. For example, manufacturing of the PS Capacitor - an EC used as a starter for diesel locomotive engines which was quite large with energy of up to 45kJ and voltage level up to 200 kV and time constant is to be less than a second.

The next innovation in the field of EC came with the design to replace the coin-cell batteries which were very successful in the solar-powered wristwatch. Today, a new design which is a spiral-wound configuration was designed targeting electric vehicles and HEVs. The spiral wound is rated at 2,000 F with 2.3V. It has a low cost with low series resistance and is also used in dispels of internally generated heat-ideal for the application in a hybrid-vehicle application.

2.3 Current Scenario

There are many electronic companies that today make ECs, including Maxwell, Murata, and Tecate group. Their product is mostly used in energy and transportation solutions. Presently, there are many applications which include hybrid transportation systems, grid stabilization, utility vehicles, automotive industry, and railway traction system using supercapacitors.

Tecate Group's HC series Ultracapacitor rated at 150 F of capacitance and voltage of 2.7V and peak current 65A. DMF series exhibits the world's highest output power which hails a quick charge/discharge cycle and the ability to level peak loads for an energy-storage system. Another example of the application of a supercapacitor is in the combination with fuel cells for maximized energy storage and quick charging abilities. An example is ABB's rapid charging station that allows an electric bus to get quick charging.

2.4 Future Applications

Talking about supercapacitor's technology isn't without discussing its future applications. As the technology gets enhanced with time and getting quite close to standalone supercapacitor batteries. There has been a prototype of supercapacitor created that takes up a fraction of lithium-ion cells, making it charge more quickly and can get the recharge as more as possible nearly 30,000 and still working like new.

Also, there is a potential in using supercapacitors in textiles to develop smart fabrics and wearable electronics.

2.5 Realistic Applications

The most promising future of supercapacitor is a combination of existing energy-storage technologies with a double-layer charging interface. The technology has been continuously evolving from EC technology to existing energy-storage technology which has been successful in rapidly improving charge-discharge cycles that can enhance the performance of hybrid and electric vehicles. Many cities have been using hybrid technology for public transportation by improvement in the overall energy storage and charging cycles coupling them with the energy systems with charging stations for electric buses.

The market for electric vehicles has already hit the change in energy storage. Supercapacitor and its applications have achieved as a part of the change from the older technology getting better with time.

The realistic application of it in the FSCs is the use of it in wearable electronics and textile-based electronics.

2.6 Research

There has been quite good research focused on EDLCs and other forms of supercapacitors. There are many testing techniques to define the properties that are meant to be processed by the capacitor and can only be known by having the analysis of various tests, including CV analysis, EIS, and the GCD (chronopotentiometry) test.

Cyclic voltammetry is a widely-used electrochemical technique. It yields basic information which includes, voltage window, capacitance, and cycle life. CV plots the current that flows through the electrochemical device and the voltage being swept across the voltage range. The pair of sweeps in opposite directions is called a cycle. CV can be made to run with two different types of electronic configuration i.e. two-electrode or three-electrode cell connections. The three electrodes are:

1. Working Electrode- Electrode being tested.
2. Reference Electrode- Electrode with constant electrochemical potential.
3. Counter Electrode-Inert electrode present in the cell to complete the circuit.

The voltage swept across the device is created by the current, I, given by equation (3).

$$I=\left(\frac{dQ}{dt}\right)=C\left(\frac{dV}{dt}\right)\ldots\ldots(3)$$

where t is the time. The I-V characteristics from an ideal capacitor (no equivalent series resistance (ESR)) tested through CV show a rectangle shape loop. ESR causes a slight rise in current at scan rates and rounds the two corners. Curves thus formed during the cyclic voltammetry can be normalized by using the various scan rates, also the scan rates affect the value of capacitance for the sample being tested. It can also be used to assess the cycle life of a device by comparing the loops over 1000 of cycles.

Electrochemical Impedance Spectroscopy (EIS) has two different modes of operation, they are,

1. Potentiostatic Mode

2. Galvanostatic Mode

Both potentiostatic and galvanostatic modes control the specimen voltage and current. Talking about the results that I did get from my observation of EIS gives a plot that is known as the Nyquist plot. The plot obtained by me in this thesis is the test results of the FSCs. Firstly, the low impedance talks about the high-frequency rates, so it can be observed that frequency decreases as we follow the curve from the origin to the right-most corner. Secondly, the values of the impedances show a negative value showing it to be capacitance to be negative reactance. Lastly, the shape of the spectrum particularly the semi-circle part which can quickly make you understand the system you are dealing with and measuring.

GCD test is carried out to know about the specific capacitance of the fabricated device. Particularly known as the chronopotentiometry test carried out to know the cycle life and the part of how the FSCs respond to the charging and discharging of it and knowing its time.

Chapter 3: Supercapacitor Electrochemistry

Electrochemistry is one of the most complex interdisciplinary fields with important field applications. This chapter has the intent to provide the basic understanding of the field as will be required for better understanding the experiments and results that were conducted through this research project. The primary importance of electrochemistry for a supercapacitor is to know the underlying electrochemical process which allows the functioning of the device. There are many electrochemical methods that are used in the fabrication of the electrodes (conducting polymers) and electrolytes (solid or liquid electrolytes).

3.1 Electrochemical Cell

Electrochemistry is concerned with the transfer of the charges between or across the interface of a chemical medium [24]. The two surfaces give rise to the interface: an electrode and electrolyte. An electrode is a phase where the charge is carried by electronic movement and the electrolytic phase where the charge is carried by the movement of ions.

The word electrolyte is something that signifies the liquid, but there are solid and gel electrolytes such a Nafion and sodium-alumina. Almost all the electrolytes are made by dissolving a salt in a solvent; however, you can find a solvent-free electrolyte called an ionic liquid. An interface arises between the electrodes and electrolytes. To investigate a single interface in isolation, the electrochemical technique is based on the electrical path be closed, a least of two electrodes needed. This collection of the interface makes an electrochemical cell.

A basic electrochemical cell has a combination of electrolytes with two electrodes. Electrode compromises the interface with the electrolyte is known as working electrode (WE). On the other hand, the electrode which completes the electrical conducting part is known as a counter electrode (CE). All the electrodes do not have the same physical and chemical compositions, which is said to be the measurable potential difference between electrodes. Potential is regardless of the current flow which arises due to potential differences between the electrodes. The most important interface of interest is only due to the working electrode-electrolyte interface.

To study the interface of the working electrode-electrolyte interface, a third electrode is introduced known as the reference electrode (RE) added to the system. The reference electrode is made of constant composition so that the potential remains fixed. This helps to study the characteristics of the working electrode and electrolyte interface. The redox couple is used in the reference electrode to determine the reference potential.

3.2 Electrochemical Potential

The cell potential is defined to be at zero energy level conventionally. The energy of charged particles from the infinite distance from the interface is considered to be zero. The term electric potential is associated with the moving of charged particles from infinity to across charged interface is referred to as Galvani Potential (it's the potential measured in volts as opposed to energy measured in joules).

3.3 Ion Transfer

There are three basic ways for the transfer of ions: migration, convection, and diffusion. Convection is not important in case when we are discussing the concepts of batteries and supercapacitors. A saturated electrolyte is used and diffusion does play an important role for more electrolytes as there is a concentration gradient when taking into consideration for batteries and supercapacitor. Migration is something that is defined by ion movement due to the potential difference between two electrodes and its effect is not that significant.

In the area where the electrolyte and electrode approach, there is a physical configuration of an electrode that causes the concentration gradient. The permeability of the electrolyte or the electrochemical reaction consumes ions. This is the region where both migration and diffusion play an important role in the movement of ions.

3.4 Comparison of Electrochemical Capacitor and Battery

Both batteries and electrochemical capacitors have the same configuration of having two electrodes in an electrolyte.

The energy that is stored in EDLCs is stored directly in the form of electrostatic energy across the double layer. The main concept of supercapacitor or electrochemical capacitors is to get higher energy density. The most recent supercapacitor technology also does not have energy density as compared to the latest batteries.

3.5 Comparison between Supercapacitor and Battery

Table 3.1 Comparison Table of Supercapacitor and Battery

Sr. No.	Battery	Supercapacitor
1.	Electrode materials decides its medium or higher energy density	It usually has lower energy density but it also depends on electrode material
2.	Low power density	Higher power density compared to battery
3.	Short cycle life (far below 1000 cycles)	Longer cycle life (as many as thousand cycles)
4.	Shorter lifetime (degradation and reconstruction of active material)	Longer lifetime (except corrosion and other factors related to current collector)
5.	Electrolyte conductivity changes depending on chemical properties of cell reactions	Electrolyte conductivity decreases during the charging due to ion adsorption.

Chapter 4: Fiber-Based Supercapacitor

Sustainability and efficient utilization of energy on a broad scale make it necessary to make rapid progress and providing upgrades in energy harvesting, conversion, and storage system. Advanced applications of supercapacitors include powering portable and wearable electronics, for which the supercapacitors are required to be flexible and having high energy and power prerequisites [1-5]. Fiber-based supercapacitors are considered as one-dimensional (1-D) type of devices that have a lightweight, small size, and good flexibility to be woven or sown into fabrics-textile. The main driving force for fiber-based supercapacitors is their flexibility and multi-functionalities in addition to high capacitive performance. FSCs according to functionalities, especially focus on the material selection, assembly methods, electrochemical and mechanical properties.

4.1 Basics of FSCs

4.1.1 Device Structure

FSC the same as the conventional capacitor which comprises two electrodes separated by an electrolyte which is an electrically insulating separator but ionically conducting a medium. FSCs are primarily assembled in four types of structures they are as described in figure 4.1.

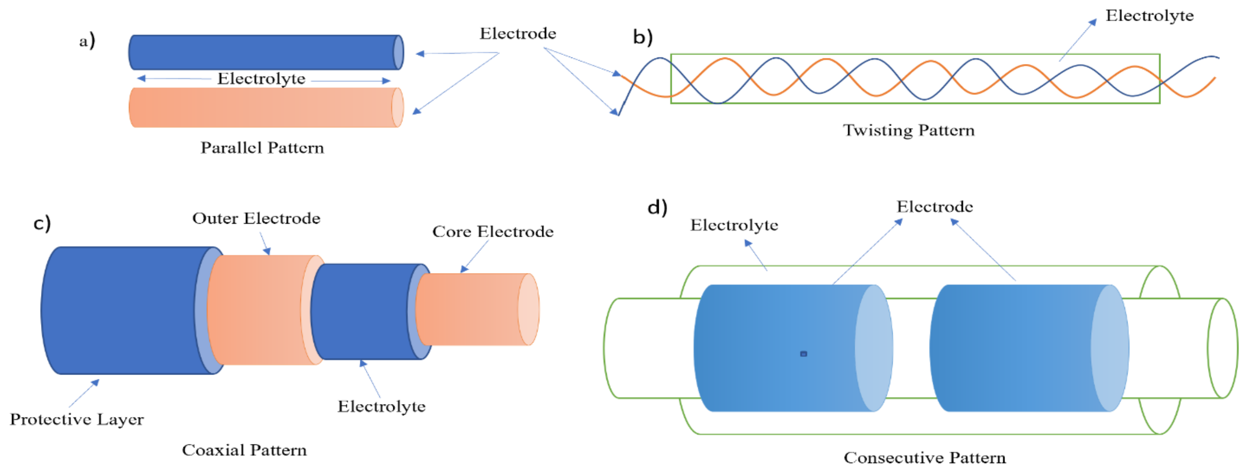

Figure 4.1 Schematic Diagram Showing FSCs in Different Structures.

1. Parallel type: Fiber-shaped electrode (FSE) each on side-to side with the electrolyte as separator between them.
2. Twisting type: FSEs twisted together with the electrolyte as the separator between them.
3. Coaxial type: Core FSE wrapped by another electrode with an electrolyte between them.
4. Consecutive type: FSEs confronted to each other covered by an electrolyte.

Regardless of the type of FSCs, two fiber-based electrodes should be close enough with no direct contact and flexible deformations of the electrode are the factor about which the care must be taken. In type (a) there are two parallel electrodes with the electrolyte between them as an ionically conducting medium with the least risk of short circuit. Type (b) twisting FSEs so as to improve the performance of the FSCs, but the chances of the electrodes getting short-circuited are increased. In type (c) there is the use of core electrode and outer shell with the electrolyte in between them as a medium thus improving the capacitance due to high utilization of electrode material [6-7]. In this type, the volume utilization of the active material is more than the twisted type [8]. This method also has a high risk of electrode getting in direct contact leading it to short circuit more risk compared to the twisting pattern. In type (d), consecutive pattern, this pattern is supposed to be not utilizing the entire performance of the active material due to the physical separation between the electrodes.

4.2 Performance Parameters

There are many performance parameters used to characterize FSCs, including energy density, power density, capacitance and cycle stability, etc. The term capacitance is defined as the measure of the stored electrical charges being charged up to 1V which is stored by the device. The capacitance of the device when the electrodes are connected in series is given by equation (1).

$$\frac{1}{C} = \left(\frac{1}{C+ve}\right) + \left(\frac{1}{C-ve}\right) \quad (1)$$

where C_+ and C_- are the capacitances at the + and - electrodes can also be calculated by the galvanostatic charge-discharge method which can be calculated using equation (2).

$$C = \left(\frac{I}{\left(\frac{dV}{dt}\right)}\right) \quad (2)$$

In the equation above *I* is the discharge current, *t* is the discharge time and *V* is the operation potential. $\frac{dV}{dt}$ is the slope of the discharge curve. When the condition curve being linear. For the non-linear curve, half of the maximum potential (*V max*) instead of full potential during a time period given by (*V max- (1/2) V max*)/ (t_2-t_1). The capacitance can also be calculated by the CV test given by equation (3).

$$C = \frac{Q}{2V} = \frac{1}{2}Vv \int_{V-ve}^{V+ve} I(u)\, du \quad (3)$$

Q signifies the charge accumulation at the electrodes, *v* being the scan rate and *V* representing the potential of the higher (*V* +ve) and lower (*V* -ve) side limits on integration.

Specific capacitance is said to be dependent on quite a good number of measuring quantity-based mass (g), volume (cm^3), area (cm^2), or length (cm) to be taken into consideration while defining the specific capacitance.

$$Cs = \frac{C}{Bd}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Bd representing mass/volume/area/length of different components like an electrode, active material as a whole device. Rate capability is a term coined in order to describe capacitance retention which is said to be CV test (high scan rates), or (GCD) test (large current densities), this term is directly in relation to the electrical conductivity of the electrodes. For example, carbon is better than metal oxides to perform better under both the CV and GCD tests.

There is also a significant term known as cycle stability which is defined from the GCD test and known for repeated charging and discharging cycles.

In regard, to the flexible FSCs which potentially be integrated with the textile industry having its application in wearable electronics. The performance stability under various mechanical deformations can be made like twisting, bending, weaving, and many more.

4.3 FSCs with Different Scaffolds

4.3.1 Carbonaceous Fiber

This material is used from the early stage due to the properties such as chemical inertness and low cost. This is one of the most significant materials and popular in the early stages of manufacturing the electrical double layer capacitor (EDLCs). With the evolution in technology, new forms of electrochemical carbon came into play such as CNT (carbon nano-tube) and graphene, and so on. There are three basic types of carbon nanofiber (CNF), graphene fiber (GF), and carbon fiber (CF). Amongst all the types, CNFs are the most flexible with good overall mechanical performance and higher conductivity. GFs are mainly fabricated with a wet chemical process with lower conductivity and poorer tensile strength. The most outstanding property of CFs having excellent conductivity and mechanical properties [9].

There are also some carbon-based fibers derived from synthetic polymer and natural fiber with the help of high-temperature carbonization in the fabrication of FSCs [10-11].

4.3.2 Metal Wires

This is also a good candidate for fiber due to its higher electrical conductivity that is important for the transport of charges and internal resistance thus facilitating the electrochemical process. Many flexible metal fibers are used as FSEs in FSCs such as SS (stainless steel), Cu, Pt, and Titanium. Their electrical conductivity is two to three orders of magnitude higher than the carbonaceous fiber.

4.3.3 Synthetic Polymer Fibers (SPFs)

SPFs are used in every common domain of day-to-day life which constitute most of the clothes we wear. They are used in FSEs for energy storage system due to lightweight, flexibility and well-developed weaving technology [1,12]. They are intrinsically insulating against the fundamental requirement of electrode material. The most common strategy is to have a conductive coating of either carbon films or nanoparticles of metal.

4.3.4 Natural Fiber

These have also been used as FSCs. The significant factor of natural fiber is to gain sufficient conductivity due to its insulating nature. The most used natural fiber in FSCs is cellulose-based yarns like cotton. Natural fibers are flexible and fibrous material with the structure of fibrils and microfibrils bundled together. Microfibrils show strong adsorption capability to water or another polar solvent [13]. Using similar approaches cellulose-based yearns like linen, bamboo and cotton are processed to FSEs for flexible and stitchable FSCs [14]

4.4 Conclusion

This chapter talks about the FSCs and their type of fabrication technique. It also describes to us the different types of fiber that can be used to fabricate the device. Coming chapters will discuss the different types of methods that can be used in order to fabricate the device and their properties in terms of specific capacitance that can be calculated.

Chapter 5: Stitching Fiber-Based Supercapacitor

5.1 Introduction

Textile-based electronics have been one of the emerging technologies with a potential impact on wearable and flexible electronic devices. [15-18] The technology that builds fiber-based electronic devices with the use of substrates such as cotton, CNT yarn, and metal fibers, etc. In comparison to the conventional devices, this emerging technology has shown quite better properties in some prospects. Fiber-based devices have the capability of bearing deformations in almost all dimensions and configurations. Also, another attractive feature of them is that they are easily compatible with conventional textile technology. Hence, the fabric formed can be made on with comfort on daily usage.

5.2 Conventional Textile Manufacturing Process

One of the most attractive features of fiber-based supercapacitors is that they can easily, be woven into fabric/textile using the already laid traditional textile manufacturing units. Researchers have also developed some technique which has helped in getting long length fiber supercapacitors [19-21].

Recently, Zheng and his co-workers reported that they did produce 500 m long Ni-coated cotton yarns on outer was deposited graphene to get a fiber electrode to make supercapacitor [19].

In another experiment done by Peng et a., they fabricated FSCs in a stripe shape. CNT/PANI composites were used as active electrodes to fabricate the supercapacitor which showed high energy and power densities [20]. The next section in this chapter will describe us about the how is the experiment carried out by stitching technique.

5.3 Experimental Setup

5.3.1 Material

Phosphoric acid (H_3PO_4) and PVA are used in making gel-based electrolytes. This process is discussed in the final experimental section of the thesis. JAMECO (Silver-reinforced nylon 66 fiber) purchased from JAMECO Valuepro with lineal resistance of 50 Ω/m and BCP conductive thread (Stainless steel fiber blended with polyester) purchased from Sparkfun Electronics with lineal resistance of 92 Ω/m.

5.3.2 Fabrication of Manual Stitching Fiber-based Supercapacitor

Materials required for the basic fabrication of the device were the JAMECO fiber, BCP conducting thread, PVA- H_3PO_4 based gel electrolyte, and the glue gun.

The first and foremost need was the coating of the fiber-based electrode with the conducting electrolyte. Firstly, one fiber was laid on the fabric and to maintain the structure of fiber in a straight manner on the fabric, it was glued at its both ends using a glue gun. The next step was laying the first layer of gel electrolyte on the fiber. Similarly, coating the fiber that needs to be stitched on it and letting it settle down for 24 hours. After 24 hours again the fiber is coated with a second layer of electrolyte and meant to keep again for two days to get it dried up. The primary role of the second layer is to prevent short-circuiting while fabricating the device.

A manual method to stitch the electrodes over each other. The length of fiber was 10 cm, and the length of each stitch was 4 mm to 5 mm. The number of stitches was 20. It is done by using the conventional needle and thread method stitching them together in order to get the fiber-based supercapacitor. The pictures of the fiber-based supercapacitors in the experimentation section are shown in figure 5.1 and figure 5.2.

Figure 5.1 JAMECO Fiber-based Supercapacitor (Hand Stitching Technique).

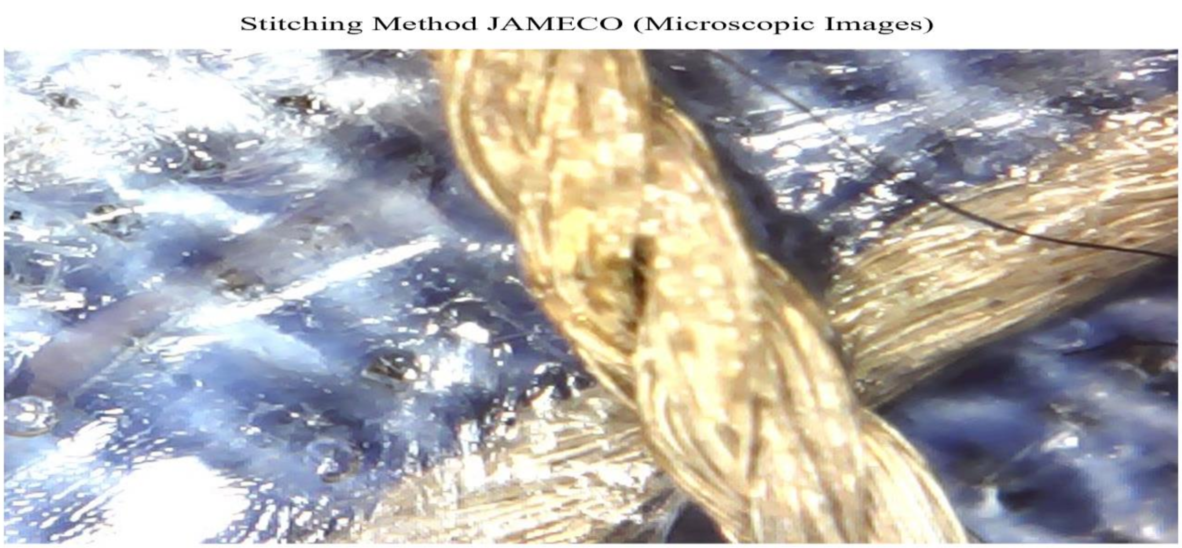

Figure 5.2 Stitching Method JAMECO (Microscopic Image)

Stitching Method BCP (Microscopic Images)

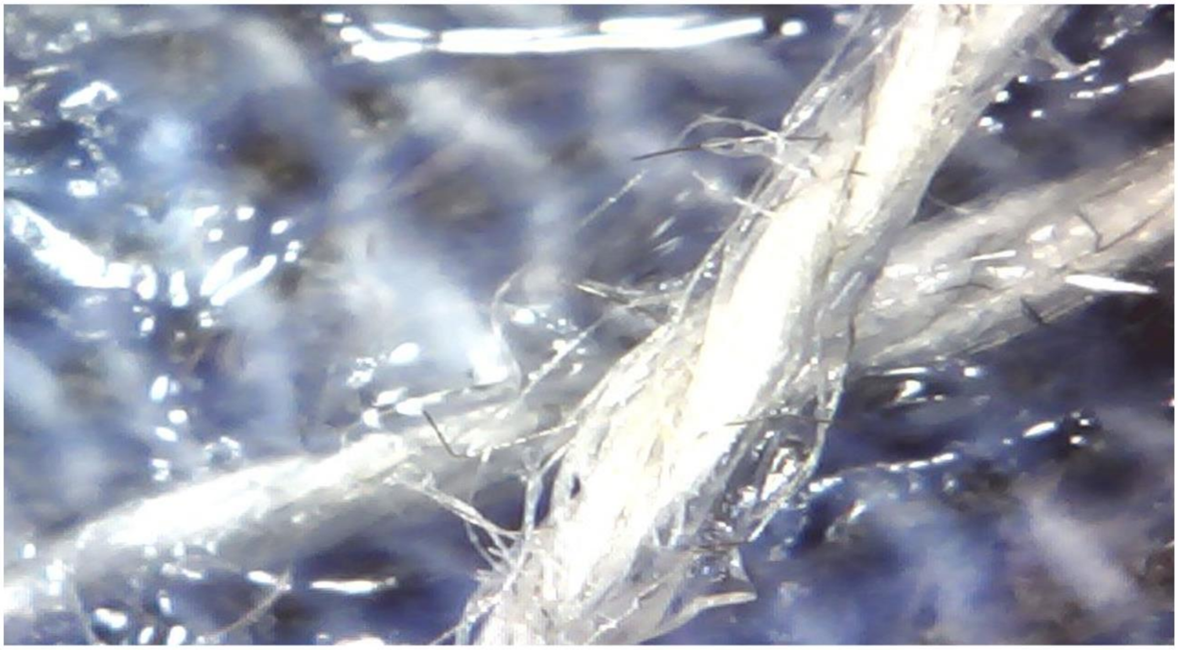

Figure 5.3 Stitching Method BCP Fiber (Microscopic Image)

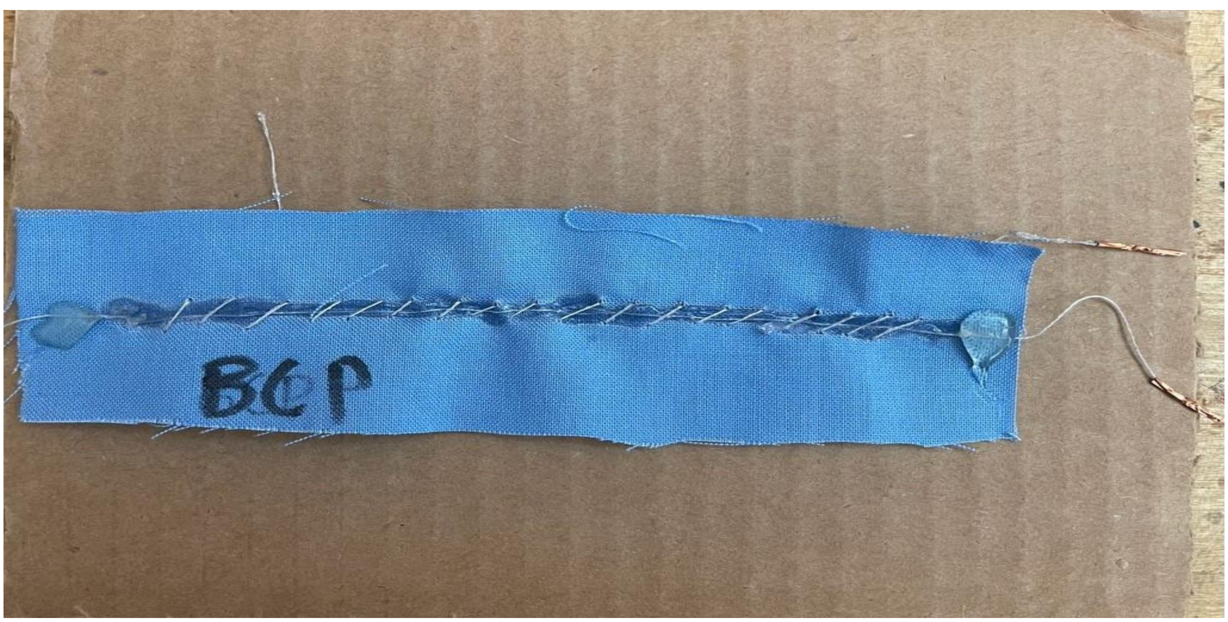

Figure 5.4 BCP Fiber-based Supercapacitor (Hand Stitching Technique).

The CV analysis of both the devices was done and on the basis of which their specific capacitances were calculated for both of the devices that were developed for testing. Below are the figures for the CV analysis for the same.

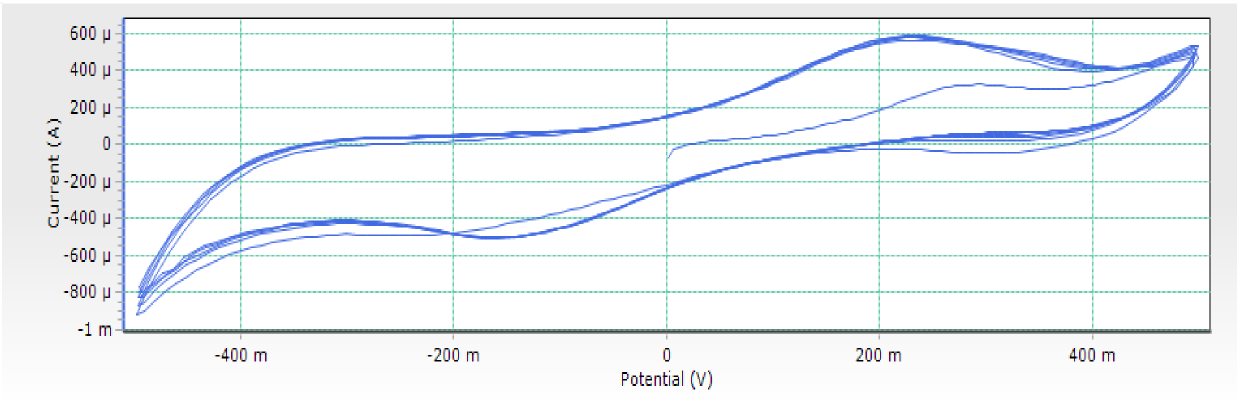

Figure 5.5 JAMECO (Day 1)

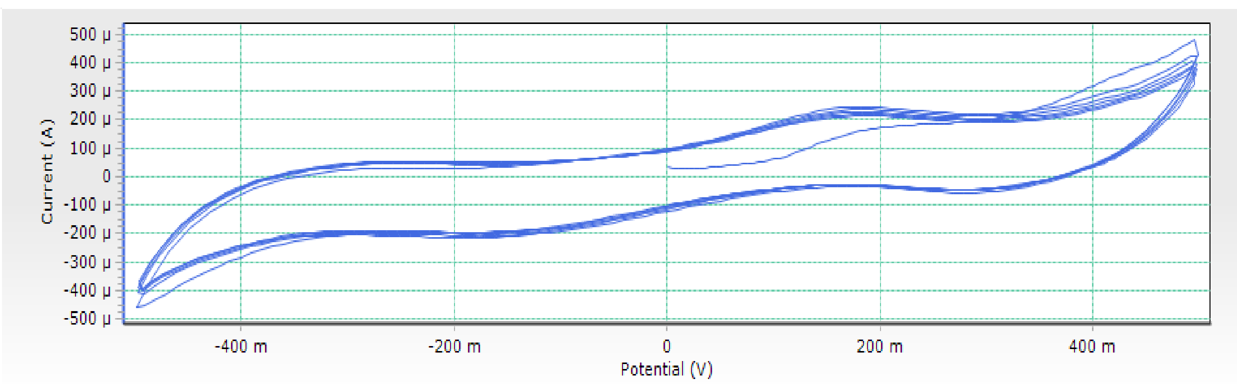

Figure 5.6 JAMECO (Day 2)

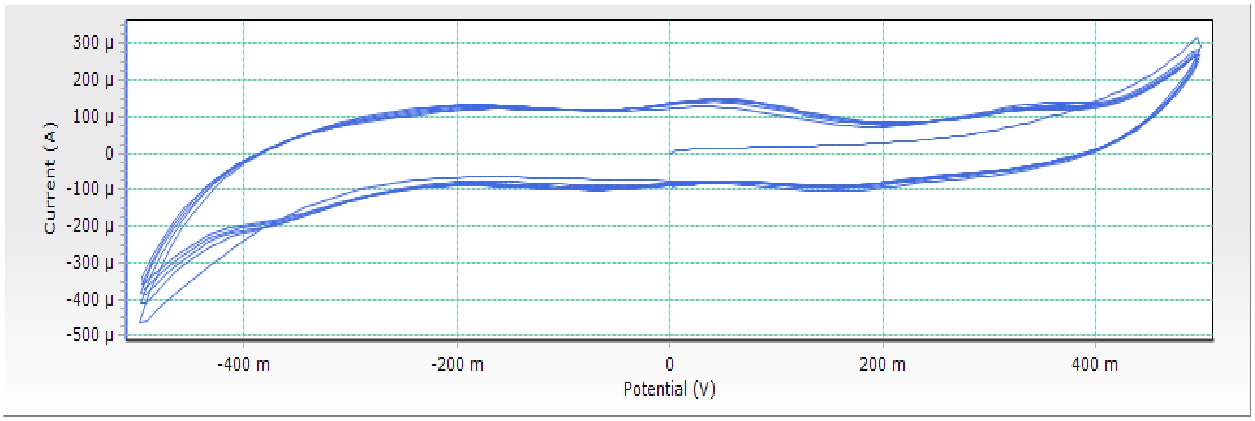

Figure 5.7 JAMECO (Day 7)

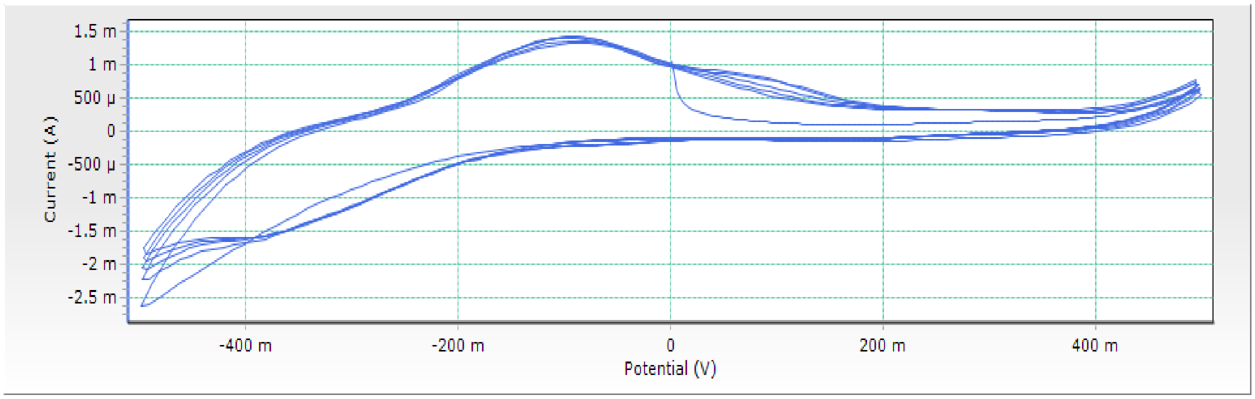

Figure 5.8 JAMECO (Day 7 after Adding Water)

The figure below shows the CV plot of BCP fiber-based supercapacitor.

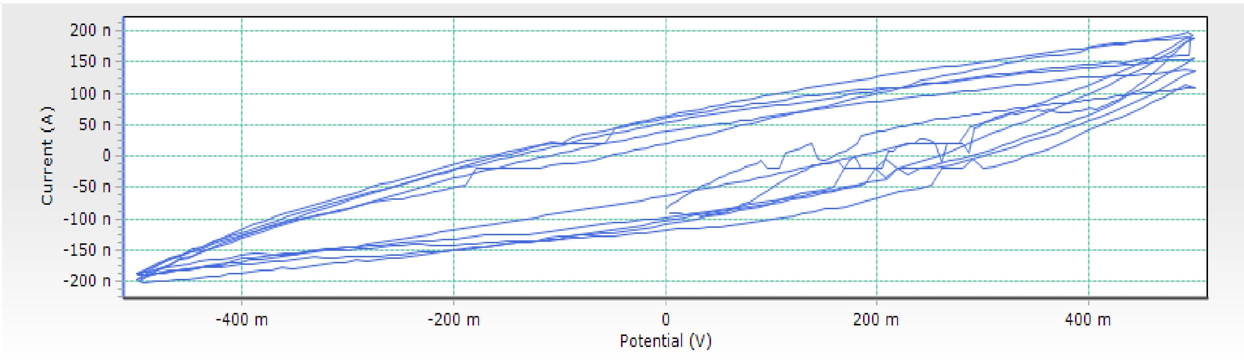

Figure 5.9 BCP (Day 1)

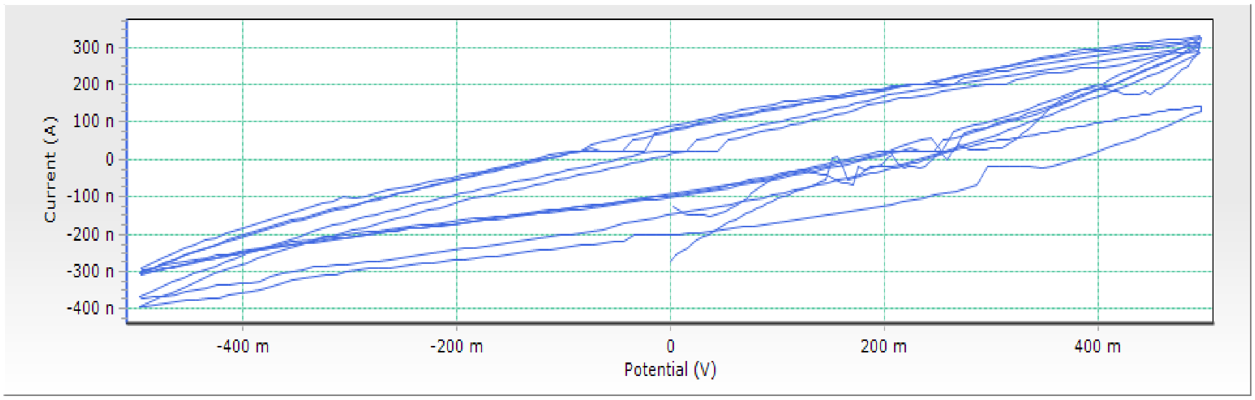

Figure 5.10 BCP (Day 2)

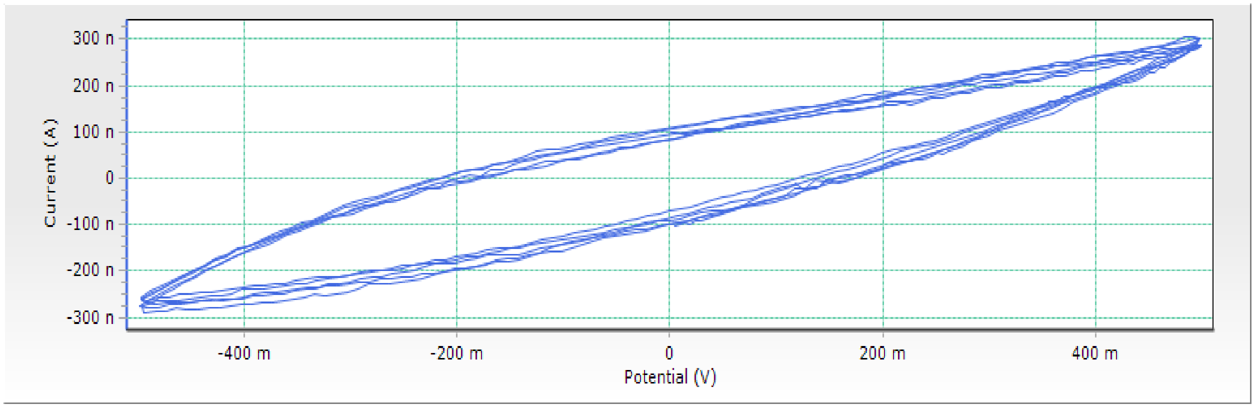

Figure 5.11 BCP (Day 7)

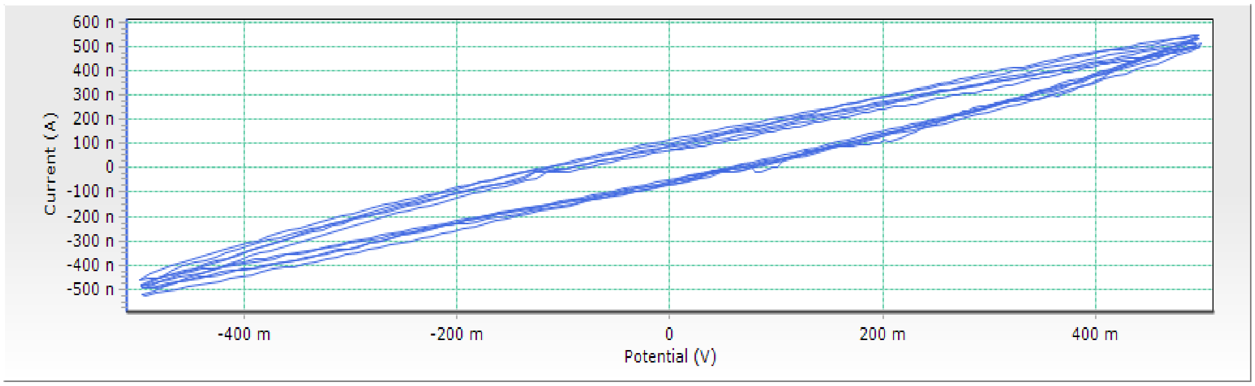

Figure 5.12 BCP (Day 7 after Adding Water)

The table 5.1 below shows the specific capacitance calculated for JAMECO and table 5.2 shows specific capacitance of BCP.

Table 5.1 Specific Capacitance of JAMECO

Segment	Scan Rates (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance (F/g)
4 (1day)	50	4.18E-04	0.405	1	2.066E-05
4 (2day)	50	2.09E-04	0.405	1	1.034E-05
4 (7day)	50	1.74E-04	0.405	1	8.607E-06
4 (7day) Add water	50	8.45E-04	0.405	1	4.173E-05

The above-obtained results clearly illustrate a lot about the capacitive nature of the device. For JAMECO it can be seen as the days pass the value of capacitance drops as the gel losses its water retaining capability until 7 days. On the seventh day, the same sample is added with drops of water, and the CV analysis is done for the same device. The device shows a good rise in the capacitive value of the JAMECO based device making its capacitance to be 41.7 µF that is almost double the value of capacitance that we did observe on day one after CV analysis.

Table 5.2 Specific Capacitance of BCP

Segment	Scan Rate (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance (F/g)
4 (1day)	50	1.21E-07	0.395	1	6.112E-09
4 (2day)	50	1.22E-07	0.395	1	6.184E-09
4 (7day)	50	1.32E-07	0.395	1	6.683E-09
4(7day) Add water	50	1.17E-07	0.395	1	5.900E-09

The above-obtained results clearly illustrate a lot about the capacitive nature of the BCP conducting fiber-based supercapacitors. The capacitance of the device increases by some value every day from day one till day seven. But it shows a different manner in comparison with the JAMECO as it shows a large drop in the value of capacitance after adding water on the same sample without adding water. The value of capacitance drops from 6.683 nF to 5.900 nF.

5.4 Applications

Fiber-based electronic devices are said to be used in quite a large scale of industry such as in healthcare, communication, environments, sports, security, and many more. In the past few years, there has been quite good research by textile electronics to the improvement of already existing technologies including solar cells, nanogenerators, transistors, diodes, etc. [22-23] The word textile electronics suggest that something that has to be of cloth and worn on the human for the human body. In fact of that device should be lightweight, possess high performance, and should bear mechanical deformations.

5.5 Conclusion

This chapter was all about the hand stitching technique that was used in order to calculate the specific capacitance and know about the difference that we will be able to see from the twisting technique. There are many more properties that need to be taken care of while forming FSCs. The next chapter makes us learn about aging as a property that makes a difference in the value of specific capacitance of FSCs.

Chapter 6: Capacitance Aging

This chapter talks mainly discuss about the twisting technique that is used in-order to learn about the capacitance of the device as the device starts getting aged.

6.1 Experimental Setup

The experimental setup for this part of the thesis is the twisting method used in order to calculate and observe the capacitance of the device with ageing. The aligning of the JAMECO and BCP with the help of toothpicks and buttons.

6.2 Observation

The experiments were carried out in this chapter were to see the effect of the capacitance of the FSCs as the devices were kept to age for some days and it's capacitance is measured.

6.2.1 JAMECO

Figure 6.1 is the analysis for the CV- Curve which shows as the day pass the specific capacitance of the JAMECO goes on reducing and after the third day the device gets short-circuited which is due to regular testing and applying current on the electrode ends which is due to the silver lining on the surface of the electrode. The peak that appeared on the third day is a result of the redox reaction that takes place.

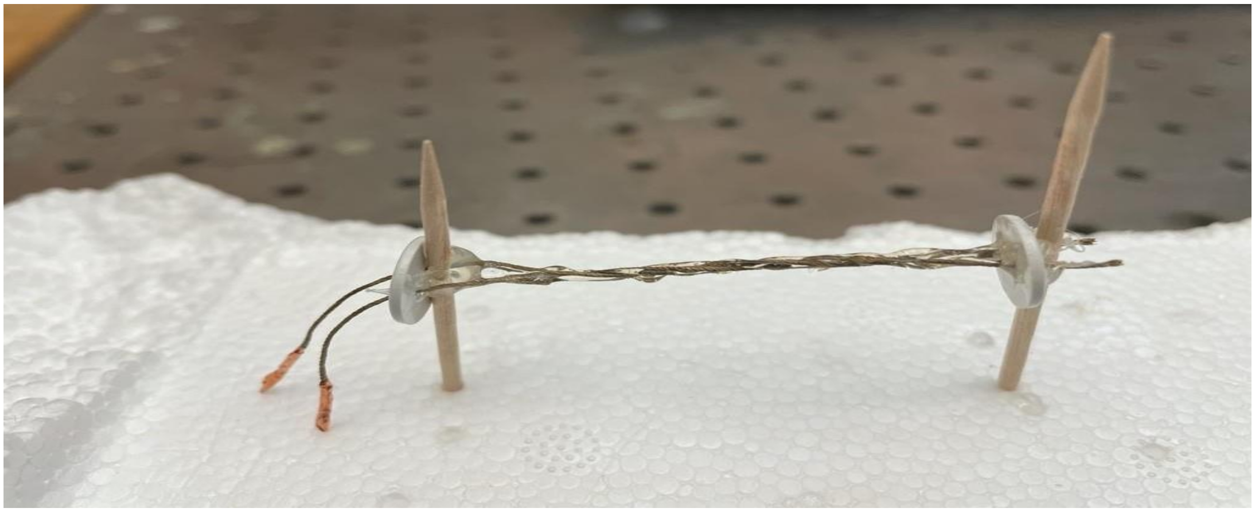

Figure 6.1 Twisted JAMECO

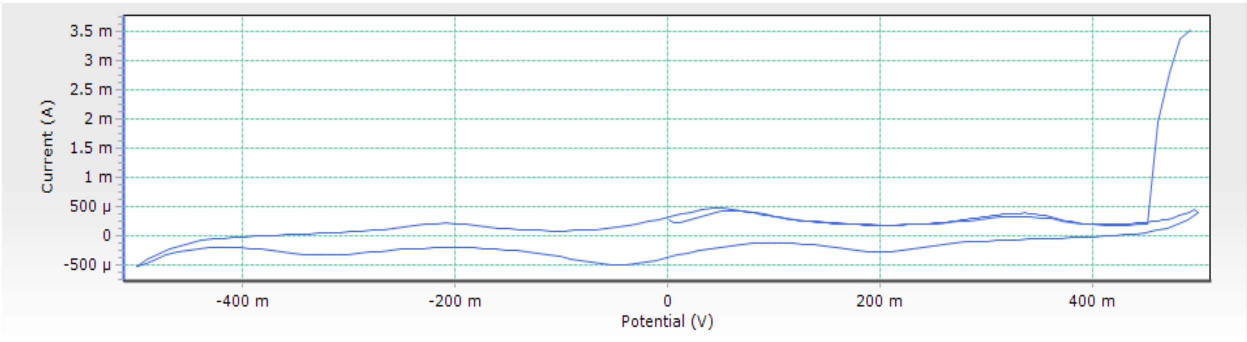

Figure 6.2 JAMECO (Day 1)

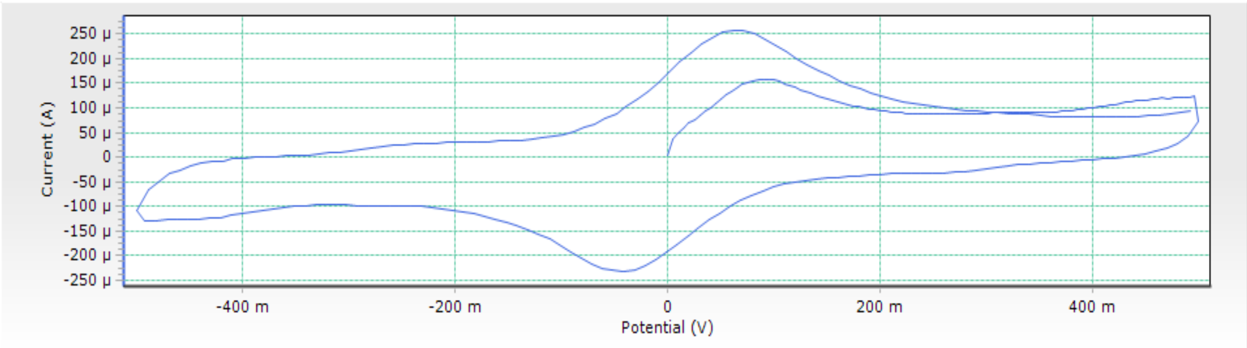

Figure 6.3 JAMECO (Day 2)

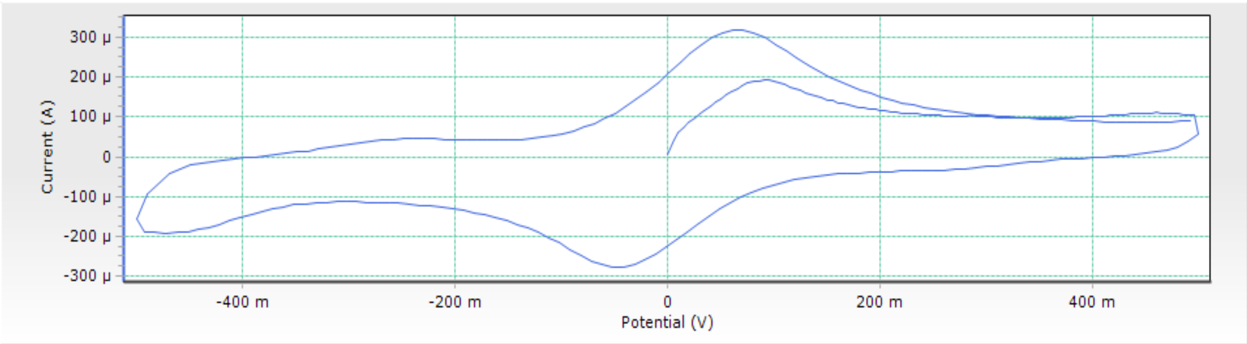

Figure 6.4 JAMECO (Day 3)

Table 6.1 Specific Capacitance of JAMECO

Segment/Day	Scan Rate (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance (F/g)
4/ day1	50	4.58E-04	0.2375	1	3.8534E-05
4/ day2	50	1.66E-04	0.2375	1	1.3987E-05
4/ day3	50	2.04E-04	0.2375	1	1.7147E-05

6.2.2 BCP Conducting Fiber

Figure 6.2 and figure 6.3 show the CV characteristic of BCP in the form of FSCs. It can be observed that the very first day when the device is tested 0.7 nF but as the result of capacitance on the second day there is an increase in the value of capacitance 11 µF followed by an increase till day 5 and then a sudden decrease in the value of capacitance to what it was calculated on the first day. On day seven the device was tested and it got reduced its capacitance lot on the same day few drops were sprayed and the device was tested again and it did show a good increase in the value of capacitance making the capacitance of the device reach 31 µF.

Figure 6.5 Twisted BCP

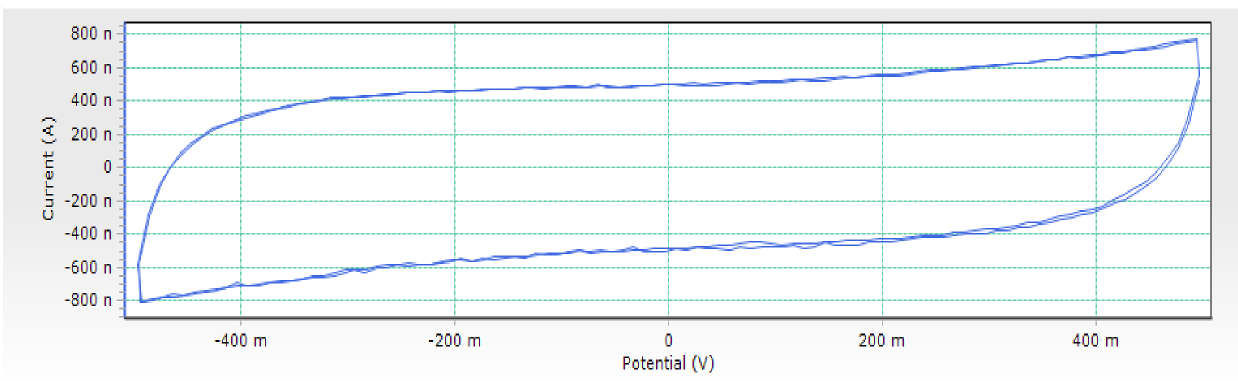

Figure 6.6 BCP (Day 1)

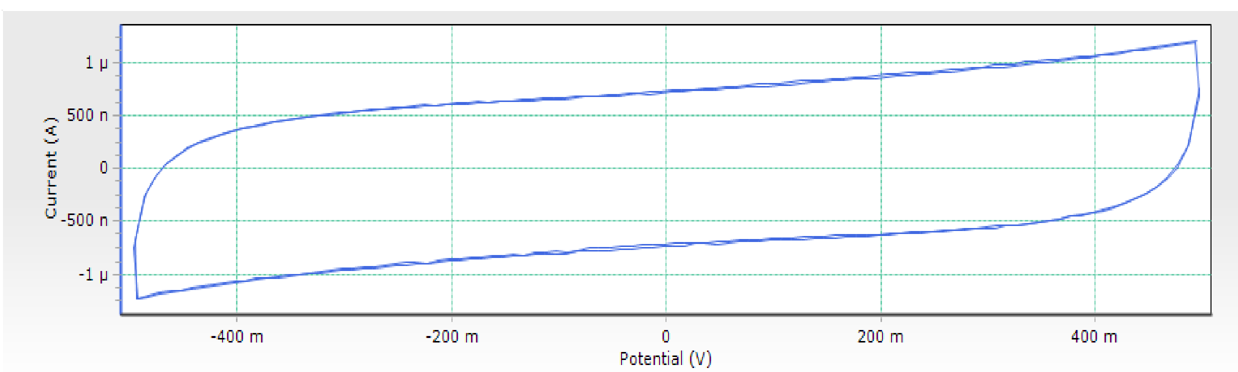

Figure 6.7 BCP (Day 2)

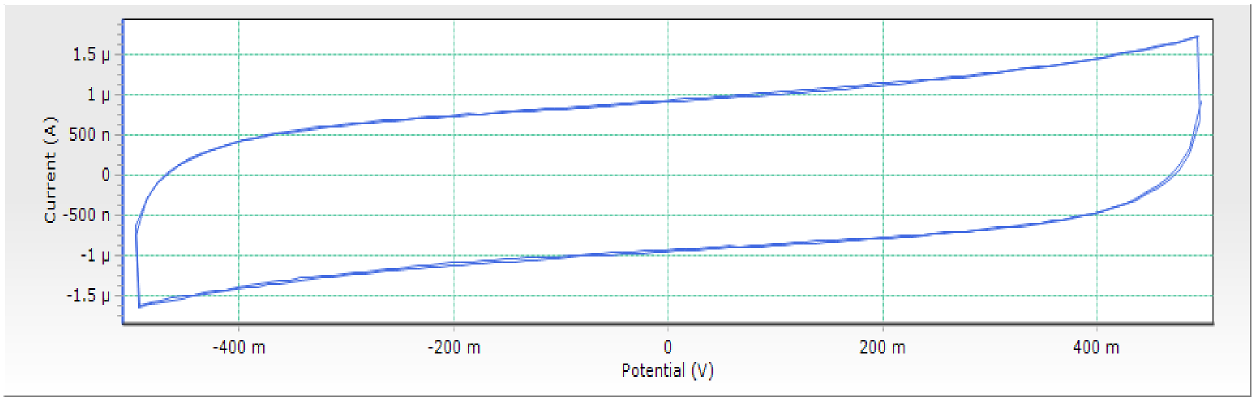

Figure 6.8 BCP (Day 3)

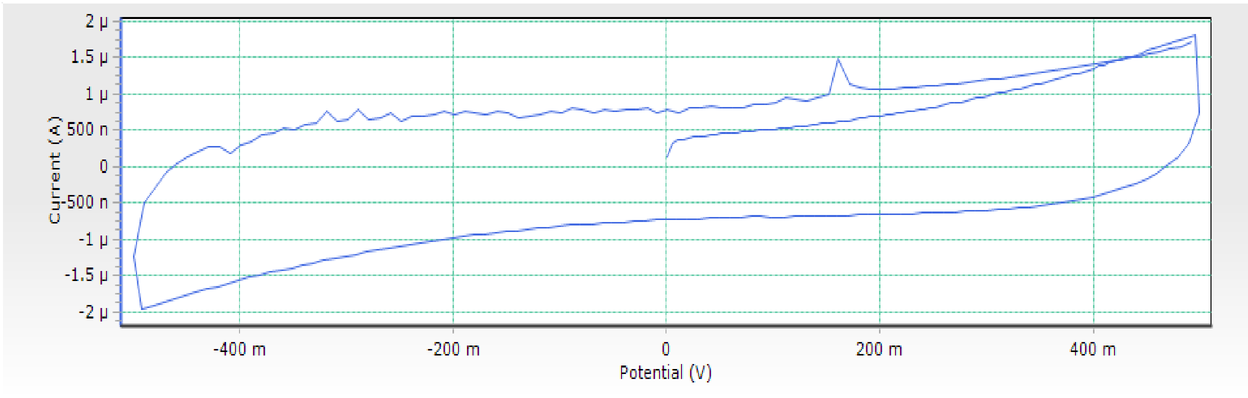

Figure 6.9 BCP (Day 4)

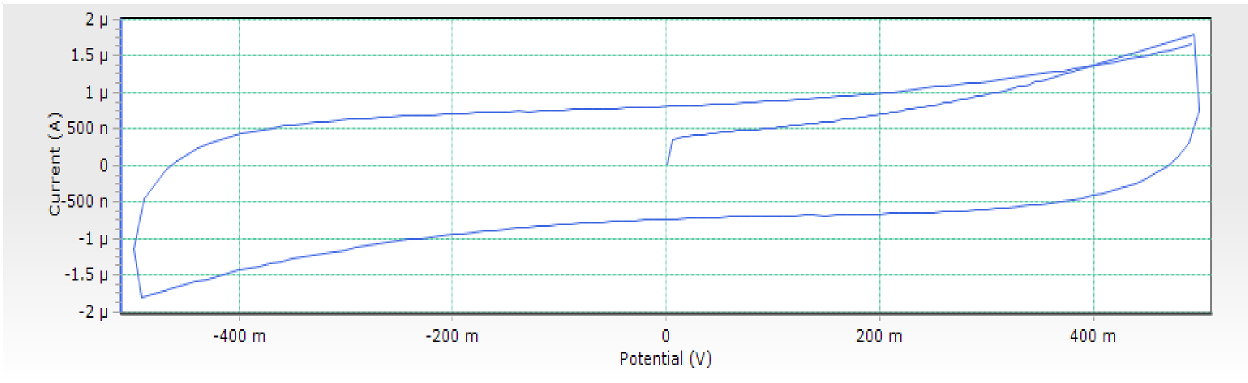

Figure 6.10 BCP (Day 5)

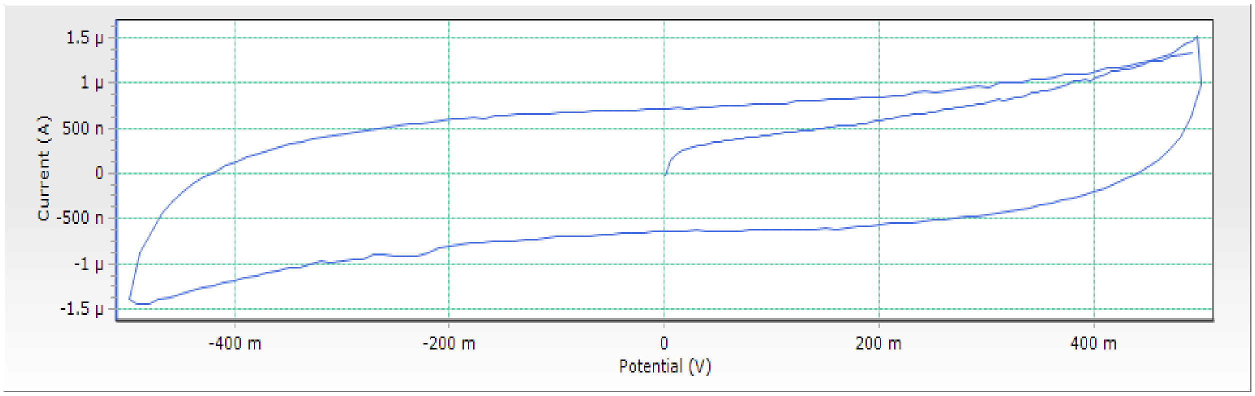

Figure 6.11 BCP (Day 6)

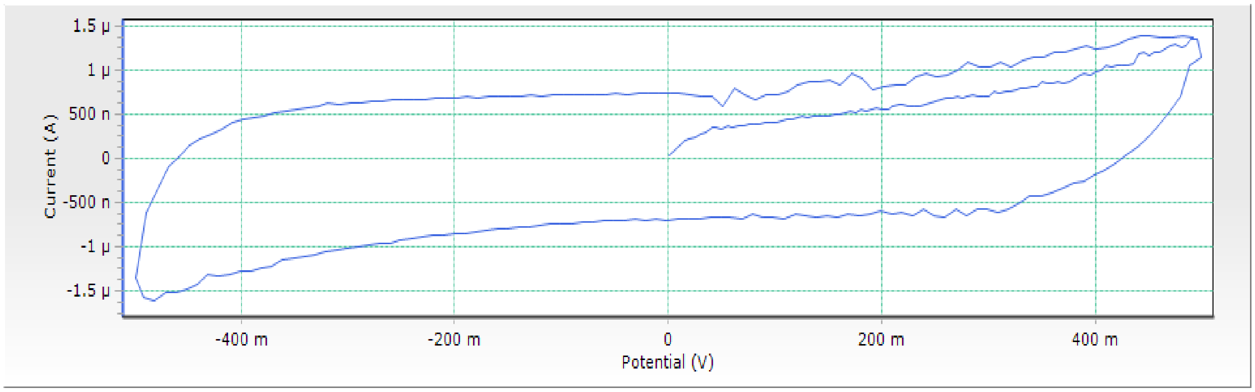

Figure 6.12 BCP (Day 7)

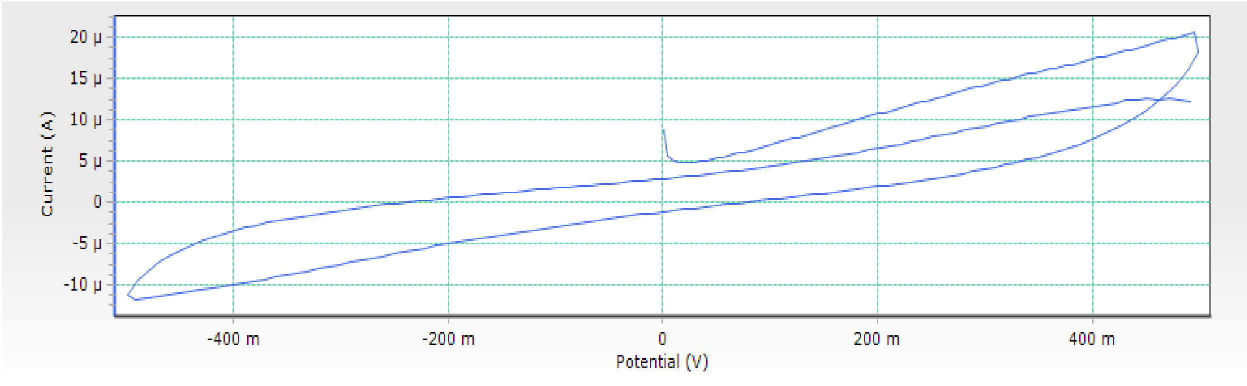

Figure 6.13 BCP (Day 7 after Adding Water)

Table 6.2 Specific Capacitance of BCP

Segment/Day	Scan Rate (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance (F/g)
4/ day1	50	9.53E-07	0.2575	1	7.3996E-08
4/ day2	50	1.44E-06	0.2575	1	1.1184E-07
4/ day3	50	1.79E-06	0.2575	1	1.3891E-07
4/ day4	50	1.72E-06	0.2575	1	1.3335E-07
4/ day5	50	1.79E-06	0.2575	1	1.3902E-07
4/ day6	50	9.49E-07	0.2575	1	7.3708E-08
4/ day7	50	9.70E-06	0.2575	1	6.3172E-08
4/ day7 with water	50	4.02E-06	0.2575	1	3.1246E-07

6.3 Conclusion

This chapter mainly discusses how the aging of the electrolyte with days passing affects the stitched FSCs. Basically, what happens to the value of capacitance how it gets increased and decreased with the days passing. The value of capacitance changes after spraying the drop of water. The coming chapter is the core for my thesis talking about the technique for twisting fiber and studying the capacitive nature of the device for the number of turns and analyzing its specific capacitance.

Chapter 7: Twisting Fiber-Based Supercapacitor

7.1 Preparation of Electrolyte

The Materials required for the preparation of the gel electrolyte are H_3PO_4 (Phosphoric Acid), PVA (Polyvinyl Alcohol), DI Water (De-Ionized water).

7.1.2 Process

The PVA/ H_3PO_4 polymer gel electrolyte was prepared by mixing 2 ml of H_3PO_4, 3 gm of poly (vinyl alcohol) in 20 ml deionized water. Then the solution was made to be heated at 90℃ and 450 rpm constant stirring till the time we find the solution becomes clear. Then the gel is covered with a parafilm and allowed to settle for 8 days and is bought to use on the same day for preparation of the sample.

7.2 Materials

PVA and H_3PO_4 were purchased from Sigma-Aldrich. JAMECO conductive thread (silver-coated nylon 66 fiber) with a lineal resistance of 50 Ω/m was purchased from JAMECO Valuepro. JL conductive thread (stainless steel fiber) with a linear resistance of 92 Ω/m, and BCP conductive thread (stainless steel fiber blended with polyester) were purchased from SparkFun electronics and BCP, respectively.

7.3 Fabrication of Supercapacitor Using Conductive Thread

Conductive threads used for the fabrication of the supercapacitor are as follows with their detailing.

7.3.1 Fabrication Process of Supercapacitor Using the Conductive Thread

Materials required for basic fabrication of the supercapacitor were done using the technique which required the use of a couple of buttons, toothpick, and glue gun. The threads are passed through the buttons on both sides by making bifurcation with the use of toothpicks and then is passed from the other side of the button and sealed by the instant glue from the other side. Then the thread is stretched and sealed on both the side and one of the side has an extra opening so as to separate the threads from each other in order to separate them from getting short-circuited.

The electrolyte is applied to the fiber and the fiber is left overnight letting it be dry so that can be used for testing the very next day. After 24 hours the thread then again applied the fresh electrolyte and then is twisted keeping one of the ends fixed. The turns are made by twisting the toothpick. The turns are made according to the number of turns required per experiment.

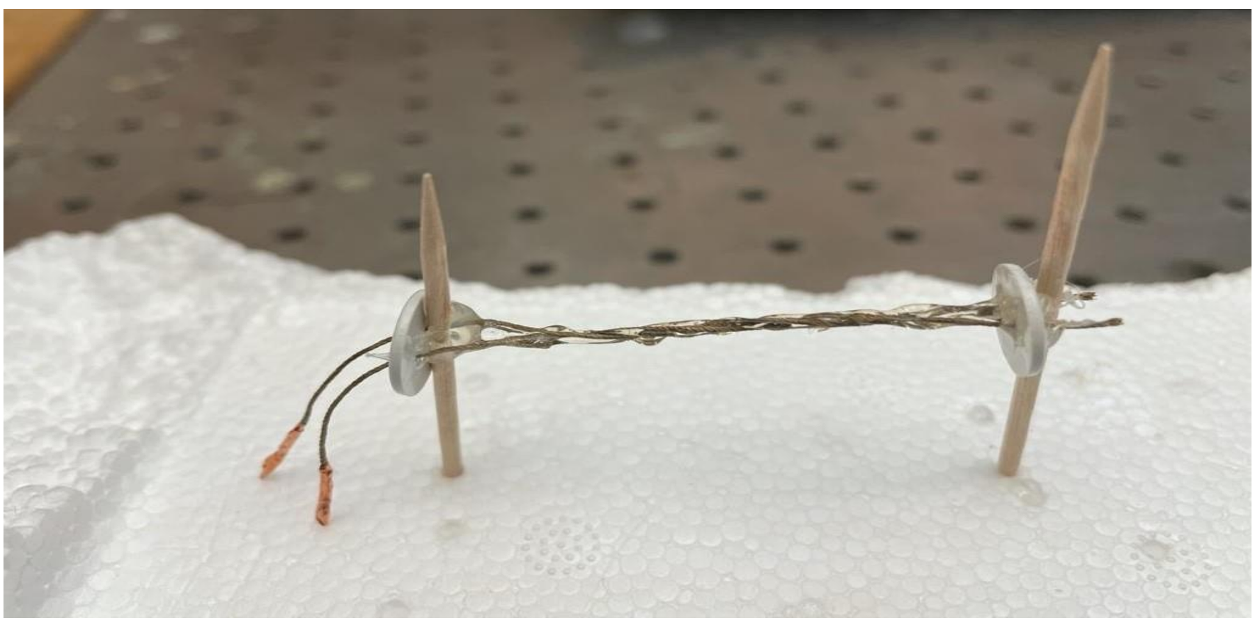

Figure 7.1 Twisted JAMECO

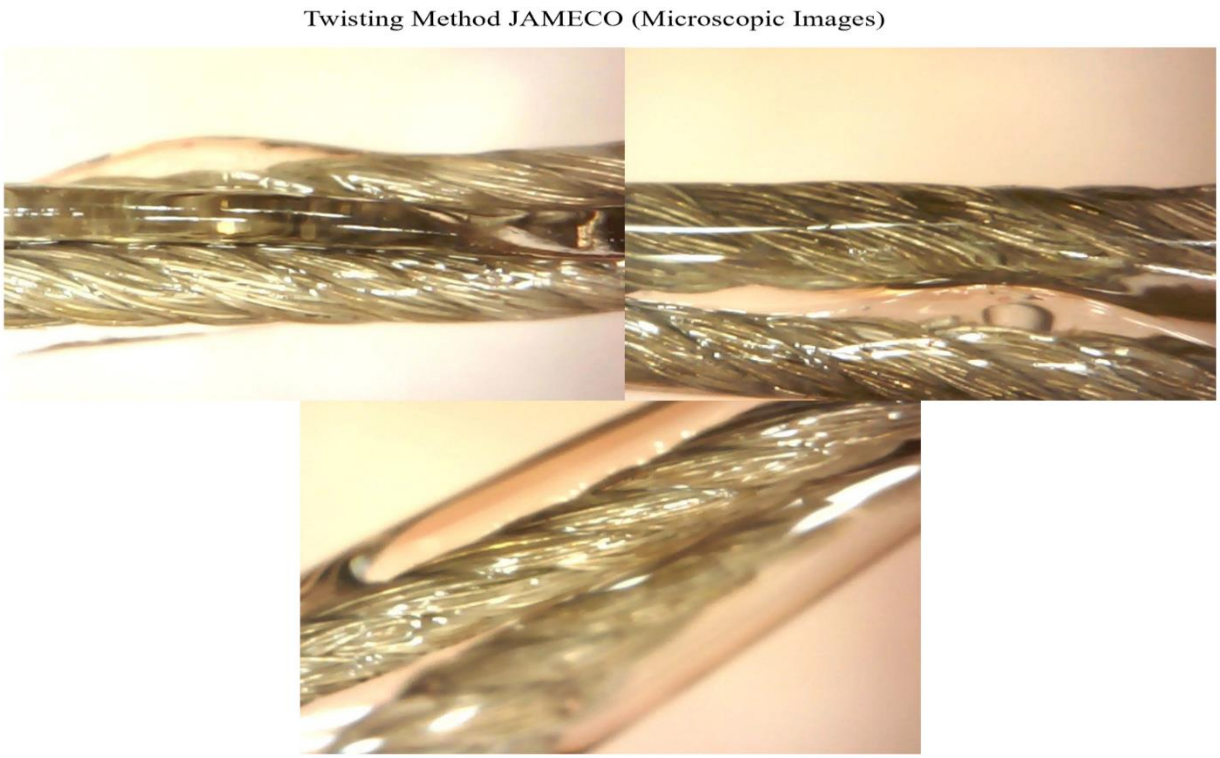

Figure 7.2 Twisted JAMECO (Microscopic Images)

Figure 7.3 Twisted JL Fiber

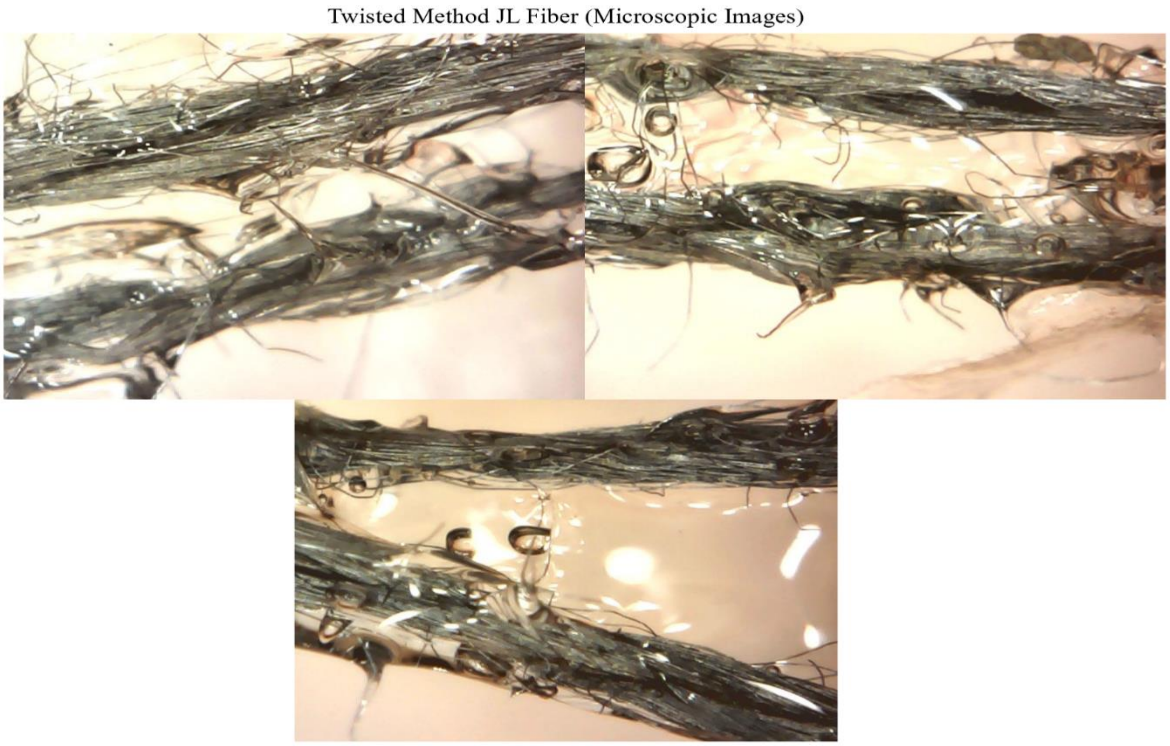

Figure 7.4 Twisted JL Fiber (Microscopic Images)

Figure 7.5 Twisted BCP Fiber

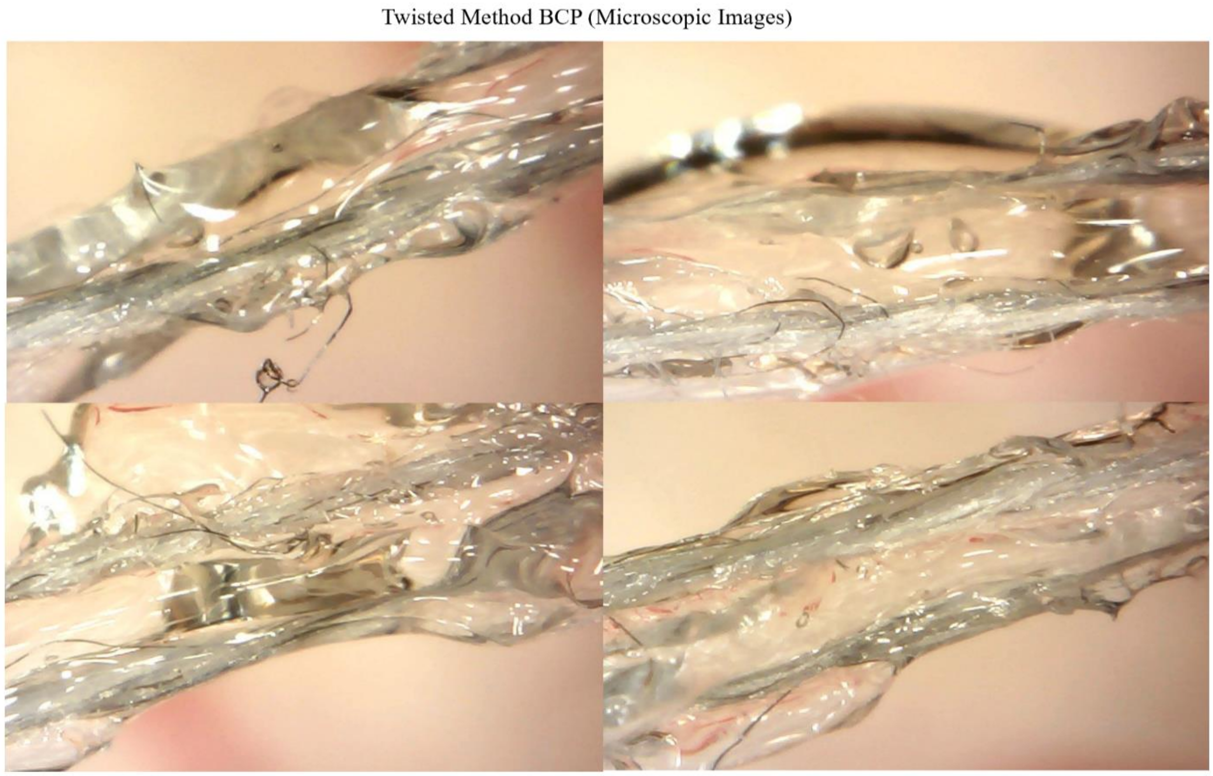

Figure 7.6 Twisted BCP Fiber (Microscopic Images)

7.4 Tests Performed

The various test performed on the fabricated FSCs for calculation of the specific capacitance of the capacitor. The three different tests performed in the experiments are the CV test, GCD test and, EIS test. The test performed has different importance in their self.

1. Cyclic Voltammetry – It is one of the most important and widely used electrochemical technique. It yields the basic information about the capacitive electrochemical cell including.

a. Cycle life

b. Capacitance

CV plots the characteristics of an electrochemical cell as the current is meant to flow as the voltage is swept across the voltage range. Pair of sweeps in opposite directions considered a cycle. It is defined as the plot of current and voltage versus time. CV is said to run with two electrodes and also the three-electrode cell connections. The method that we are using is the two-electrode method which is very common and has the involvement of reference and counter electrode connected to the one side of the capacitor and the other side with the working electrode. The experiment for the cyclic voltammetry is carried out for all three fabrics for the different number of turns.

2. GCD test - Capacitors are the device used to store electric charge and energy. A capacitor can be slowly charged to the necessary voltage and discharged quickly so as to provide the energy needed. Several capacitors charged to a certain voltage level and discharged in such a way that more voltage (not energy) out of a system than it was put in. The capacitance is calculated using the excel plotting $-ln\left(\left(\frac{\Delta Vf-\Delta V}{\Delta Vf}\right)\right)$ versus time and then recording the date on a sheet and from the value of slope determine the time constant and the capacitance. The charge stored on either conductor directly proportional to the voltage the proportionality of it known as capacitance.

3. EIS test – It is a method that is used to determine the capacitance associated with the electrochemical devices. In particular there are two modes of spectroscopy: frequency sweep and bias sweep mode. The ratio of magnitude of voltage to that of current at any frequency determines the magnitude of impedance at any particular frequency. The phase difference between the voltage and current determines the phase associated with device.

The complex impedance thus obtained are represented as bode plot or as an Nyquist plot where imaginary component are plotted against real component. The plot clearly shows the point which have been plotted between frequency and reactance.

7.5 Experimental Results

7.5.1 Cyclic Voltammetry (CV) Test Results

1. JAMECO (Segment 4)

Table 7.1 Specific Capacitance of JAMECO

Turns	Scan rate (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance (F/g)
1T	50	1.61E-04	0.235	1	1.37E-05
2T	50	8.61E-05	0.235	1	7.33E-06
3T	50	1.14E-05	0.235	1	9.70E-06
4T	50	1.46E-04	0.235	1	1.24E-05
5T	50	1.70E-04	0.235	1	1.44E-05
6T	50	1.77E-04	0.235	1	1.51E-05

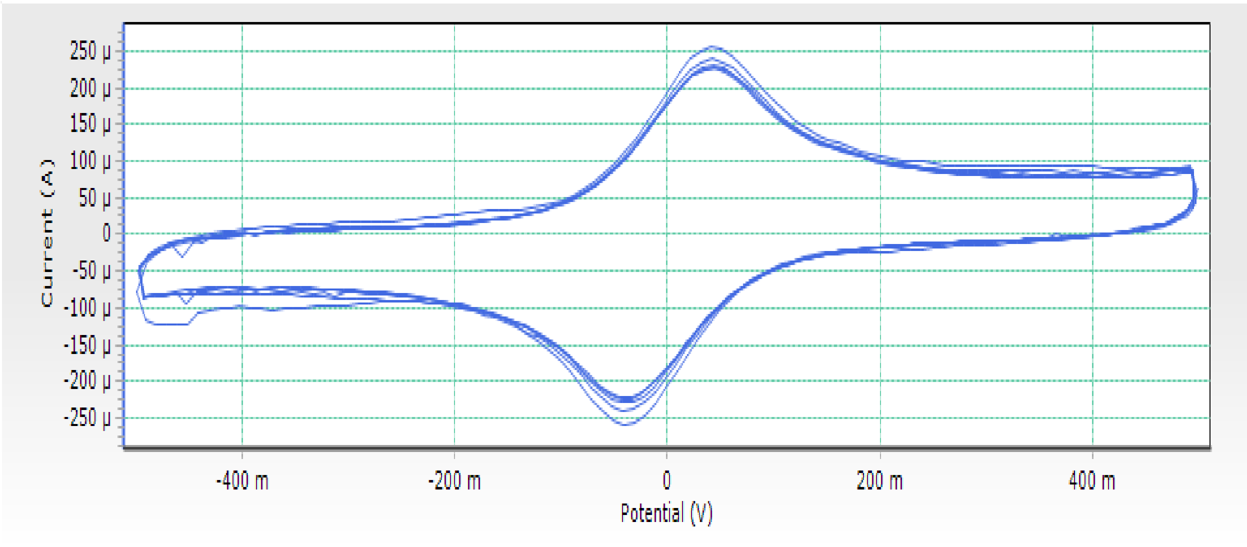

Figure 7.7 CV Curve of JAMECO

2. JL Fiber (Segment 4)

Table 7.2 Specific Capacitance of JL Fiber

Turns	Scan Rate (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance(F/g)
1T	50	2.55E-05	0.225	1	2.27E-06
2T	50	4.10E-05	0.225	1	3.64E-06
3T	50	4.17E-05	0.225	1	3.70E-06
4T	50	4.10E-05	0.225	1	3.65E-06
5T	50	4.04E-05	0.225	1	3.60E-06
6T	50	3.99E-05	0.225	1	3.55E-06

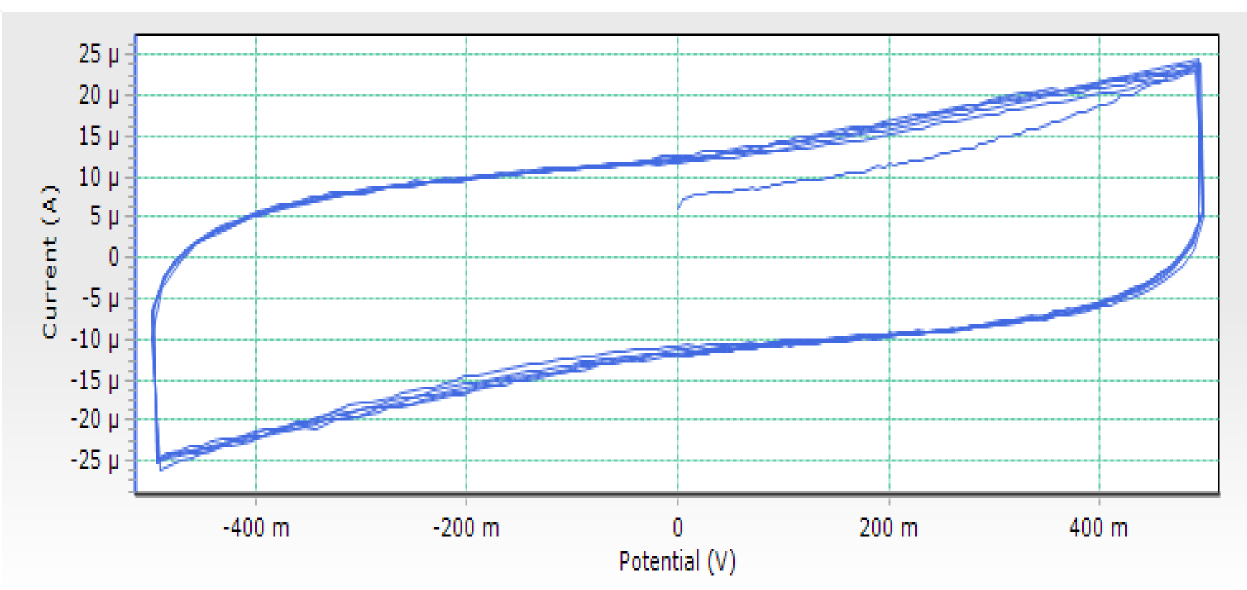

Figure 7.8 CV Curve of JL Fiber

3. BCP (Segment 4)

Table 7.3 Specific Capacitance of BCP

Turns	Scan Rate (mV/s)	Area	Mass (g)	Delta V	Specific Capacitance (F/g)
1T	50	7.66E-07	0.2575	1	5.95E-08
2T	50	5.10E-06	0.2575	1	3.96E-07
3T	50	5.77E-06	0.2575	1	4.48E-07
4T	50	6.00E-06	0.2575	1	4.66E-07
5T	50	5.63E-06	0.2575	1	4.37E-07
6T	50	6.26E-06	0.2575	1	4.86E-07

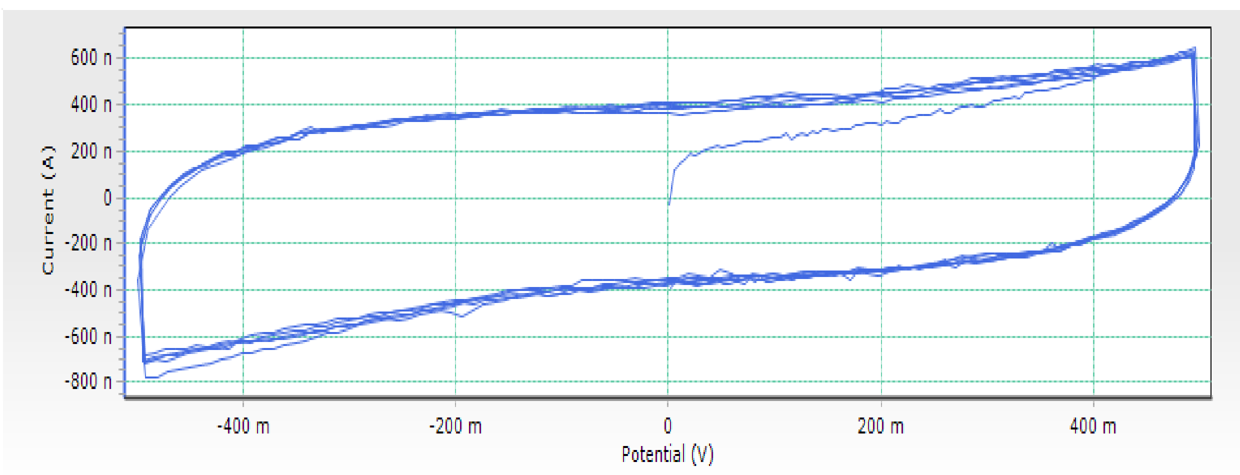

Figure 7.9 CV Curve of BCP

CV Characteristics tells us about the charging and discharging of the supercapacitor and the stability related to curves of the CV plot that yields basic information about a capacitive electrochemical cell including voltage window, capacitance, and cycle life and is considered to be having a quite comprehensive description.

The CV tests were held for all the devices that were fabricated from single turn to six number of twisting turns in the potential range between -0.5 V to 0.5 V at the scan rate of 50 mV/s. The voltage range is made to be on the lower side because of the presence of water in the electrolyte and avoids its electrolysis. Figure 7.1 shows the Fiber-based supercapacitor on the JAMECO thread with 1 to 6 twisting turns. There are two pair redox peaks that are observed in CV curves: one pair around 0.0V and the other at 0.35V. The largest peak of current was observed near the 0.0 V and the second peak was not visible as the device being tested from 3 to 6 turns of twist. The redox peaks suggest the pseudocapacitive behavior that emerged from the surface of the redox reactions, which is due to the fact of the presence of silver structure of the fibers. The weaker peaks being are likely due to the active behavior of the gel electrolyte. The most significant aspect in the CV curves is the increase in the redox amplitude which is due to the increasing number of turns which directly impacts the increase in the capacitance of the device. The CV results of the device based on JL Fiber-based device showed the symmetrical rectangular shapes further the capacitance curve graph is increased with the second turn and thereafter there is no such major increment in the capacitance with the increase in the number of turns. The capacitance is said to be limited after the second turn. The CV loop of BCP fiber-based capacitor with one twisting turn to be narrow (T1). For T2 to T6 weaker redox peaks were observed with a significant increase in the capacitance area as compared to the first twisting turn. The specific capacitance of supercapacitor with JAMECO, JL and, BCP at their highest value (T6) was 15.1 μF/g, 3.55 μF/g and, 0.485 μF/g respectively.

Specific Capacitance has been calculated for all the three fiber-based supercapacitors which clearly states that the JAMECO is said to have the maximum capacitance followed by the JL Fiber and the least capacitance to be possessed by the BCP conducting threads.

7.5.2 Galvanostatic Charge/Discharge Test

1. JAMECO (Segment 6)

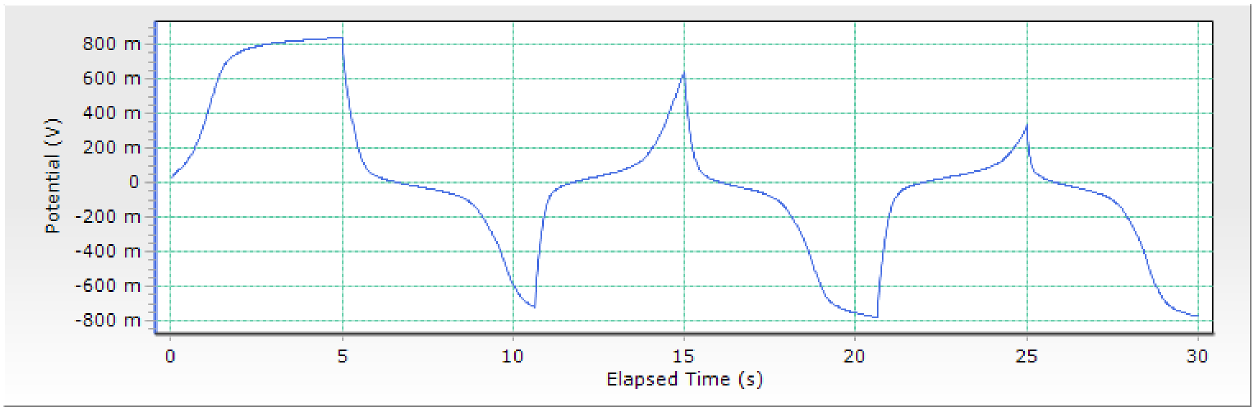

Figure 7.10 Charge/Discharge of JAMECO

2. JL Fiber (Segment 6)

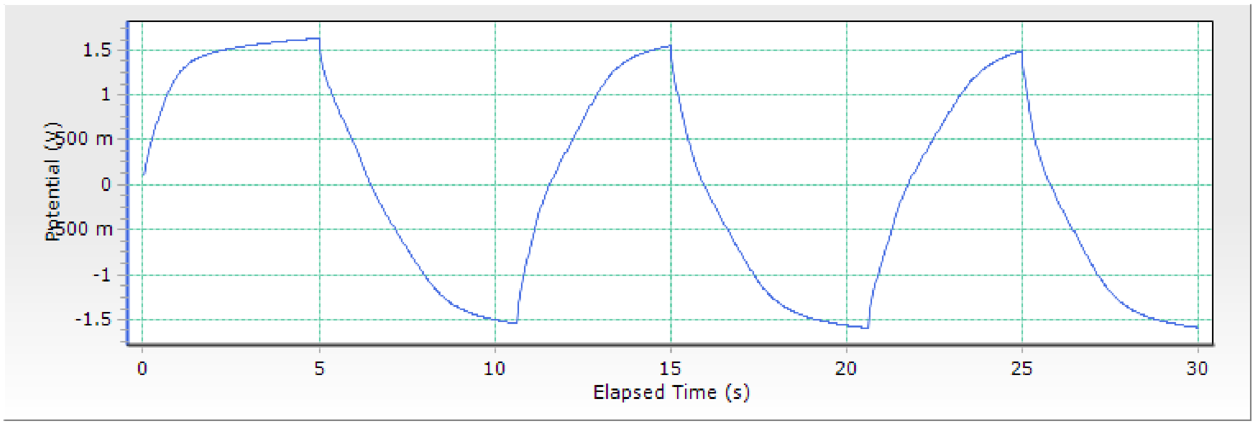

Figure. 7.11 Charge/Discharge of JL Fiber

3. BCP Conducting Fiber (Segment 6)

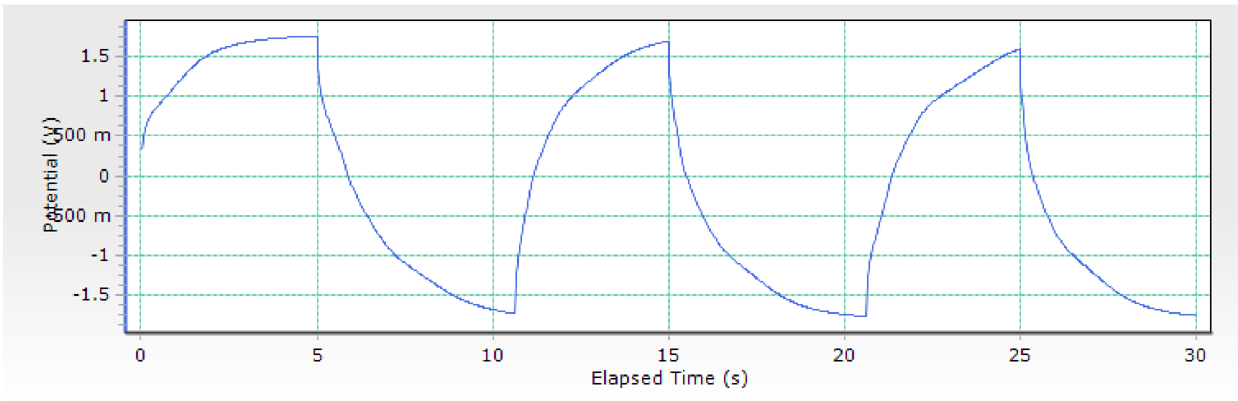

Figure 7.12 Charge/Discharge of BCP Fiber

The GCD test that was performed on the fiber-based capacitors its results have been seen above graph. The technique which was used by the device was the chronopotentiometry (CP) technique with a constant current range of 0.5 mA during its charge and -0.5 mA during its discharge cycle. Lower capacitances observed in the CV analysis made to reduce in the current range to charge and discharge cycle range of 0.05mA. Faradaic reaction in the JAMECO gave rise to higher turns in it, which made it a non-linear curve with the voltage profile possessed by it. JL and BCP give linear characteristics in their charging and discharging cycle.

7.5.3 Electrostatic Impedance Spectroscopy

1. JAMECO (Segment 6)

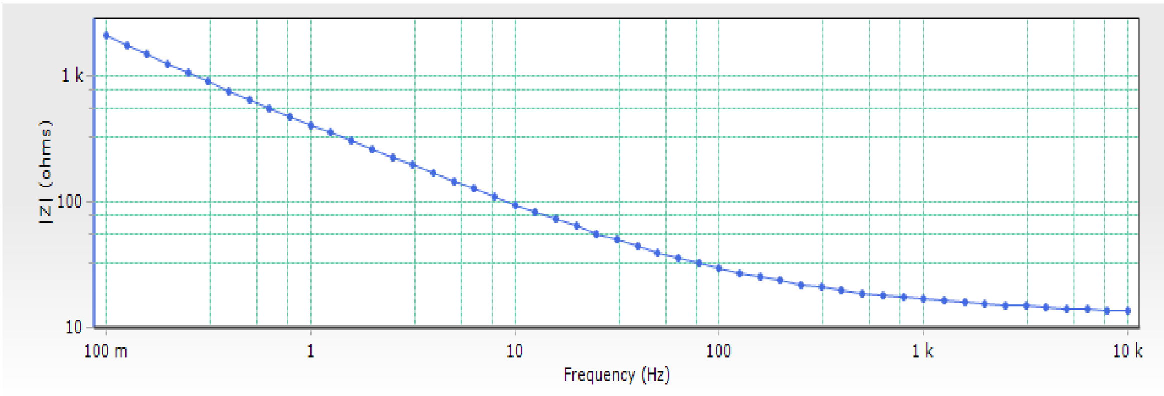

Figure 7.13 EIS of JAMECO

2. JL Fiber (Segment 6)

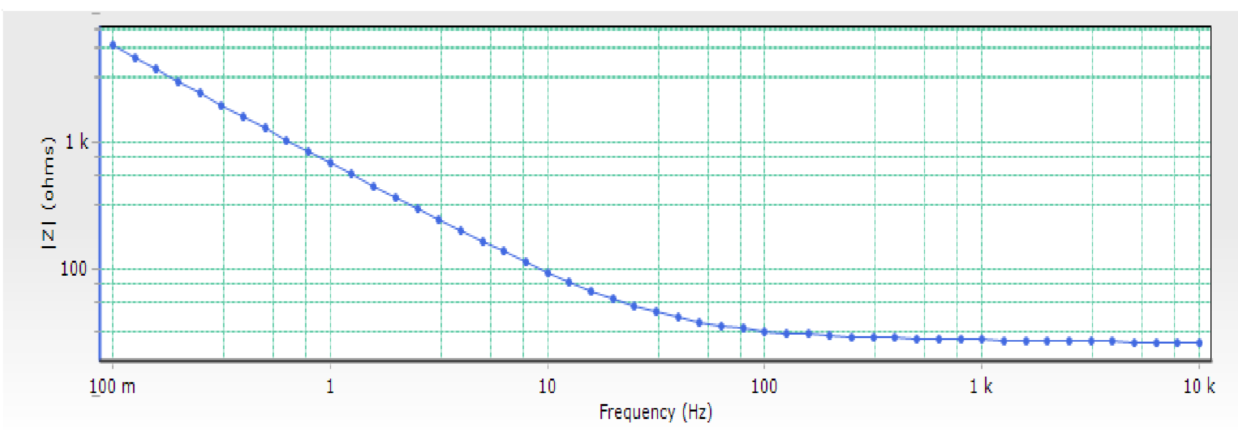

Figure 7.14 EIS of JL Fiber

3. BCP Fiber (Segment 6)

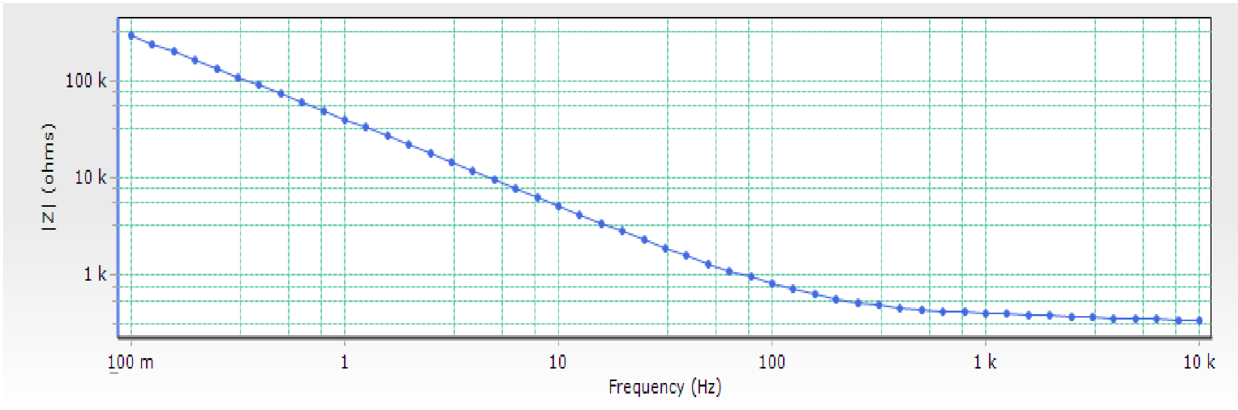

Figure 7.15 EIS of BCP Fiber

The EIS test was performed in order to study and determine the capacitance and limitations that were associated with the property of the supercapacitor. The mode used to determine the behavior in our case study is the frequency sweep mode. In this method the small amplitude of the voltage is applied across the supercapacitor for a wide range of frequency and the current drawn is measured. The measured plot for the device is plotted and represented in form of a Bode plot where magnitude and phase are represented as the function of frequency. The capacitive behavior is shown by JAMECO as it possesses its capacitive behavior for a large range of frequency followed by BCP and JL fiber having a less difference in their capacitive behavior possess for the frequency range. But as the frequency range increases the FSCs start losing their capacitive nature converting themselves to show more of resistive nature with the increase in frequency.

Chapter 8: Conclusion

In conclusion, using the CV test and Galvanostatic charge/discharge test, the specific capacitance of the twisted fiber with a different number of turns was calculated. The capacitance aging has also been studied in detail for the JAMECO and JL Fiber and they have been analyzed. A manual technique to sew is also performed by knitting the fibers with needles and conducting thread. The result can thus now be used to design more efficient wearable and textile-based electronics.

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