PEDOT:PSS Charge Storage Devices Integrated into Textiles for Smart Textile Application

Sheilla Atieno Odhiambo

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Supervisors

Professor dr. ir. Lieva Van Langenhove
Department of Textiles
Faculty of Engineering and Architecture
Ghent University (UGent)

Professor dr. ir. Gilbert De Mey
Department of Electronics & Information Systems
Faculty of Engineering and Architecture
Ghent University (UGent)

Member of the Examination Committe

Professor dr. ir. Luc Taerwe (Chairperson)	UGent - Belgium
Professor dr. ir. Lieva Van Langenhove	UGent - Belgium
Professor dr. ir. Gilbert De Mey	UGent - Belgium
Dr. ir. Carla Hertleer (Secretary)	UGent - Belgium
Professor dr. ir. Karen De Clerck	UGent – Belgium
Professor dr. ir. Dagmar D'hooge	UGent – Belgium
Professor dr. ir. Wim De Ferme	UHasselt - Belgium
Professor dr. John Githaiga	MU - Kenya

Contact

Sheilla A. Odhiambo

Ghent University – Department of Textiles

Technologiepark 907

9052 Zwijnaarde, Belgium

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Logic will get you from A to B.

Imagination will take you to everywhere

Albert Einstein

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Samenvatting

Systemen van intelligent textiel maken interactie tussen de gebruiker en zijn/haar omgeving mogelijk via detectie en besturing. Toepassingen zijn te vinden in sportkleding, mode van de toekomst met visuele lichtinteractie, gezondheidszorg en telemonitoring, kleding die op geluid reageert voor autismepatiënten en persoonlijke beschermkledij. Systemen van intelligent textiel bestaan uit sensoren, actuatoren, een energievoorziening, gegevensverwerkingseenheden en verbindingen voor de transmissie van signalen en/of gegevens. De energie kan opgeslagen zijn in batterijen of kan ter plekke gegenereerd worden. De batterijen die momenteel in intelligent textiel worden gebruikt zijn niet flexibel, veelal volumineus en zwaar, en kunnen het comfort van het textiel zelf niet evenaren. In dit onderzoek willen we een component creëren die geschikt is voor opslag van lading om stroom te voorzien voor intelligent textiel en die goed geïntegreerd is in het textiel. De ontwikkelde component moet bovendien licht, flexibel en betrouwbaar zijn.

Hoofdstuk 1 geeft een uitgebreid overzicht van elektrische componenten voor energieopslag (batterijen en capaciteiten) en waardeert het onderzoek van een aantal onderzoekers naar flexibele, op textiel gebaseerde batterijen en capaciteiten. Een functioneel, volledig geïntegreerde component voor energieopslag moet echter nog worden ontwikkeld. In dit hoofdstuk geven we ook een korte samenvatting van het werk van Bhattacharya *et al.* over herlaadbare textielbatterijen, waarop ons onderzoek is gebaseerd. We ontwikkelden een gelijkaardige component voor opslag van lading, op een vereenvoudigde manier en met verschillende soorten garenelektroden. We ontdekten nieuwe inzichten en beschreven die in onze publicaties.

Hoofdstuk 2 beschrijft in detail de materialen die werden geselecteerd en gebruikt voor de constructie van onze component voor opslag van lading. De materialen worden beschreven naargelang hun functie in de ontwikkelde condensator. Het materiaal dat als **elektrolyt** werd gebruikt, was polyethyleendioxythiofeen: polystyreensulfonaat (PEDOT:PSS). Drie soorten geleidende garens (met koper gecoat polybenzoxazool (PBO), met zilver gecoat PBO en filamentgarens uit zuiver roestvrij staal) werden gebruikt als **garenelektrodes** in drie verschillende componenten. Uit de beschikbare weefselvariëteiten werd een mengsel van katoen/polyester geselecteerd als **textielsubstraat**. Een smeltlijm werd gebruikt om het drielagig weefsel te lamineren

en het oppervlak van het textielsubstraat werd hydrofoob gemaakt met thermoplastisch polyurethaan (TPU). De condensatoren werden ontworpen en vervaardigd met behulp van verschillende soorten garenelektrodes.

Hoofdstuk 3 beschrijft de laad/ontlaadprocedure die wordt gebruikt om de ontwikkelde componenten te karakteriseren. Uit de resultaten werd afgeleid dat de ontwikkelde cellen een zelfontlading vertoonden. De componenten die bestonden uit met koper gecoate garenelektrodes slaagden er nauwelijks in een lading op te slaan. De componenten met garenelektrodes van roestvrij staal daarentegen deden het beter dan die met zilver gecoate garenelektrodes. Ze slaagden erin gedurende een lange tijd een lading van minstens 0.4 V te behouden, terwijl de componenten met zilver gecoate garenelektrodes ongeveer 0.2 V behaalden. De componenten met garenelektrodes van roestvrij staal konden eveneens een belastingsweerstand doorstaan. Hoe langer de oplaadtijd, hoe meer lading kon worden opgeslagen in de componenten. De componenten uit PEDOT:PSS hadden geen voorgedefinieerde polariteit, beide elektrodes konden worden gebruikt voor positieve of negatieve elektrodes en omgekeerd indien nodig. Bijgevolg mogen we de elektrodes geen kathode of anode noemen, omdat ze allebei van hetzelfde materiaal zijn gemaakt. Men kan zich afvragen waarom we voor de ontwikkelde componenten voor ladingopslag de term component en/of cel gebruiken in plaats van een “batterij” of “condensator”. Dit was een moeilijke beslissing, rekening houdend met het feit dat we zijn gestart van de gedefinieerde batterijprincipes van Bhattacharya´s *et al.* Maar aangezien we twee elektrodes gebruiken die van hetzelfde materiaal zijn gemaakt, handelen we strikt genomen met een condensator. Anderzijds konden we niet uitsluiten dat er zich elektrochemische reacties zouden voordoen in de cel, aangezien het fysieke mechanisme van ladingopslag in PEDOT:PSS nog steeds niet goed gekend is.

In hoofdstuk 4 werd de betrouwbaarheid en de stabiliteit van de ontwikkelde cel getest. De componenten voor ladingopslag werden verscheidene keren opgeladen en ontladen gedurende een aantal dagen tot ze uitgeput waren. De componenten met garenelektrodes uit roestvrij staal hebben een zekere stabiliteit en konden tot 14 cycli doorstaan van elk 7200 seconden opladen tot 1.5 V en ontladen gedurende een dag. De hoeveelheid energie die wordt opgeslagen in de cellen na het opladen is echter nog steeds erg klein omwille van de zelfontlading. We kunnen ruwweg stellen dat deze condensatoren tot 10 à 15 cycli kunnen worden gebruikt, zonder een significant verschil waar te nemen in het niveau van uitgangsspanning bij de eerste 14 cycli. Hieruit blijkt de beperkte levensduur van de ontwikkelde condensatoren in vergelijking met de conventionele die duizenden keren kunnen worden opgeladen. We ontdekten eveneens dat het onderdompelen van de cel in water een nadelig effect had op de overgebleven lading, waardoor de cel op zich niet kan worden gewassen met water, tenzij ze ter bescherming wordt bedekt/verpakt. De ontwikkelde compo-nenten presteerden slecht wanneer blootgesteld aan temperaturen hoger dan 30° C.

In hoofdstuk 5 werden verschillende merken (5) van PEDOT:PSS vergeleken voor de constructie van capaciteiten gebaseerd op textiel. Uit de analyse bleek duidelijk dat de vijf verschillende soorten PEDOT:PSS verschillend presteerden in onze ontwikkelde cellen. Bij nader inzien bleek dat de samenstelling van de polymeerdispersie en de elektrische eigenschappen erg varieerden van merk tot merk. We ontdekten dat de beste elektrolyt voor onze toepassing tot nu toe PEDOT:PSS van Ossila AI 4083 was (drop coated). De prestaties van filamentgarens uit zuiver roestvrij staal in de ontwikkelde toestellen overtroffen de prestaties van de toestellen met PBO-elektrodes bekleed met zilver.

In hoofdstuk 6 werden garenelektrodes van filamentgarens uit roestvrij staal met verschillende garendiameters gebruikt om drie verschillende PEDOT:PSS capaciteiten te ontwikkelen. Het gedrag in termen van spanningsafname van de drie verschillende soorten capaciteiten werden bestudeerd en onderzocht. Oorspronkelijk dachten we dat de spanningsafname gelinkt zou zijn aan de lineaire weerstand van het garen, maar dat bleek later niet waar te zijn. Het was dan ook moeilijk om het verschil te verklaren in de grafieken van de spanningsafname van de condensator met de dunne, de middelgrote en de dikke garenelektrodes. In ons theoretisch model wordt de garendiameter gebruikt om de kracht van het elektrisch veld rond de elektrode te berekenen. Hieruit konden we afleiden dat het elektrisch veld rond het garen sterker is bij een dun garen dan bij een dik. Dit betekent dat in ons PEDOT:PSS cel concept we met een dunner garen dat een hogere weerstand heeft geen betere prestaties konden bereiken dan met een dikker garen dat een lagere weerstand heeft.

Het doel van hoofdstuk 7 was de hoeveelheid nuttige, geaccumuleerde energie te bepalen in de ontwikkelde cel met garenelektroden uit roestvrij staal, ondanks de zelfontlading. Op een textielsubstraat werden flexibele capaciteiten gemaakt met garens van roestvrij staal als elektrodes. Het gebruikte elektrolytmateriaal was een dispersie van polyethyleendioxythiofeen: polystyreensulfonaat (PEDOT:PSS) van de firma Ossila. Het bleek niet makkelijk om de opgeslagen energie in die cellen rechtstreeks te bepalen, vandaar dat ze werd geraamd op basis van de energie die naar de voltmeter werd gevoerd. Met behulp van de vergelijking die energie linkt aan capaciteit werd berekend dat de capaciteit van de ontwikkelde cel 180µF bedroeg.

De condensator werd opgeladen op een normale manier en gebruikt om een rekenmachine (TOSHIBA LC-810) van energie te voorzien. Daarna gingen we een stapje verder en laadden de condensator op tot een willekeurige spanning van 3V gedurende ongeveer 40 minuten in plaats van de normale 1.5V gedurende 2 uren. Na de cel gedurende een voldoende lange tijd te hebben opgeladen tot 3V, bedroeg de geaccumuleerde lading in het toestel ongeveer 1.2V, echter slechts voor een korte periode. Ook in deze experimenten werd in het begin gedurende een paar seconden een hoge spanningsafname waargenomen, net zoals in de andere experimenten, waarna de spanningsafname vermindert. Ondanks de zelfontlading van de condensator kon de rekenmachine 37 seconden lang werken met de ontwikkelde cel.

Dit werk wordt afgesloten met hoofdstuk 8, dat een lijst bevat met de belangrijkste prestaties uit dit proefschrift aangevuld met aanbevelingen voor toekomstig onderzoekswerk.

Summary

Smart textile systems enable interaction of the user with his/her environment through sensing and actuation. They find application in sports garment, future fashion with visual light interaction, health and tele monitoring, sound responsive garments for managing autism, and in personal protective clothing etc. Smart textile systems consist of sensors, actuators, power supply unit, data processors and interconnects for transmission of signals and/or data. The energy supply unit can either be energy generated on the spot, or as a form of stored energy in batteries. Currently, the batteries used with smart textile systems, are non-flexible, bulky and weighty, and cannot be compared with the comfort of the textiles themselves. Therefore, this research addresses the fabrication of a suitable charge storage device well integrated into textile and that could provide power to the smart textile system. The developed devices are light weight, flexible and reliable.

We start chapter 1 by giving a wide overview of electric energy storage devices (batteries and capacitors), and appreciate the research effort made towards achieving flexible textile-based batteries and capacitors by a number of researchers. However a functional, fully integrated energy storage device is yet to be developed. In this chapter we gave a brief summary on rechargeable textile batteries which was the basis of our research. We developed a similar charge storage device, in a simplified way and with different types of yarn electrodes. We obtained new findings and reported them in our publications.

Chapter 2 discusses in detail materials selected and used in the fabrication of the charge storage devices. The materials have been discussed according to the function given in the developed capacitors. The material used as **electrolyte** was polyethylene dioxythiophene: polystyrene sulphonate (PEDOT:PSS). Three types of conductive yarns (copper coated polybenzoxazole (PBO), silver coated PBO and pure stainless steel filament yarns) were used as **yarn electrodes** in three different sets of devices. A cotton/polyester blend was selected out of the available fabric variety as the **textile substrate**. A hot melt adhesive was used to laminate the three layered fabric while the upper surface of the textile substrate was made hydrophobic using thermoplastic polyurethane (TPU). The capacitors were designed and fabricated using different types of yarn electrodes.

Chapter 3 discusses the charge - discharge procedure used to characterize the developed devices. From the results, the developed cells experienced a self-discharge. Copper coated yarn electrode devices could barely store any charge. Stainless steel yarn electrode devices performed better than the silver coated yarn electrodes devices. They maintained a charge of at least 0.4 V for a long time, while silver coated yarn electrodes devices had about 0.2 V. The stainless steel yarn electrode devices could also support load resistors. The longer the charging time, the more charge was stored in the devices. The PEDOT:PSS devices had no predefined polarity, both electrodes could be used for positive or negative electrodes and reversed if need be. As a consequence one may not denote the electrodes as cathode or anode, because they were both made from the same material. One may wonder why we are using the term device and/or cell to refer to the developed charge storage devices instead of either a “battery” or a “capacitor”. This was a difficult decision to reach at, bearing in mind that we started from a defined battery principles by another research group. But since we are using two electrodes made from the same material, strictly speaking we were then dealing with a capacitor. On the other hand we could not exclude that some electrochemical reactions could be taking place in the device, because the physical mechanism of charge storage in PEDOT:PSS is still not well understood.

In chapter 4, the reliability and stability of the developed devices was tested. The charge storage devices were charged and discharged severally for a number of days until they were worn out. The devices made with stainless steel yarn electrodes show some robustness and could withstand up to 14 cycles of each 7200 seconds charging at 1.5V and discharging for a day. However, the amount of energy stored in the devices after charging is still very low due to the self-discharge. One can roughly say that these capacitors could be used up to 10-15 cycles, with no significant difference in the output voltage level for the first 14 cycles. This shows the limited life time of these developed capacitor compared to the conventional ones which can be charged thousands of times. It was also found that dipping the device in water had an adverse effect on the residual stored charge, therefore the cell cannot be subjected to normal washing with water as it is, unless some covering/packaging is used on it to protect it. Furthermore, the developed devices performed poorly when exposed to temperatures higher than 30^0C.

In chapter 5 different brands (5) of PEDOT:PSS were compared for use in making textile based capacitors. From the analysis, it was clear that the five different types of PEDOT:PSS had different performances in our developed devices. A closer look at the polymer dispersion composition and electrical properties, indicated that these parameters were varying from one brand to the other. We found out that the best electrolyte for our application so far was PEDOT:PSS from Ossila AI 4083 which was drop coated. The performance of pure stainless steel filament yarns in the developed devices dominated the performance of silver coated PBO electrode devices.

In chapter 6, three yarn electrode of stainless steel filament yarns with different diameters were used to produce three different PEDOT:PSS capacitors. The performance in terms of voltage decay of the three types of capacitors was studied and investigated. The initial perception was that the voltage decay was related to the yarn linear resistance, but later we found out that this was not true. Therefore it was difficult to clarify the difference in the voltage decay graphs of the thin yarn electrode capacitor from the medium and thick yarn electrodes. With our theoretical model, the yarn electrode diameter was used to calculate the electric field strength around each size of yarn. From this, we could state that the electric field around the yarn is stronger within a thin yarn compared to a thick yarn. This means that in our PEDOT:PSS cell concept we could not achieve a better performing device with thinner yarn of higher resistance compared to the thicker yarns of lower resistance.

The aim of chapter 7 was to quantify the amount of useful accumulated energy in the developed charge storage device with stainless steel yarn electrodes, despite their self-discharge. Flexible capacitors were made using stainless steel yarns as yarn electrodes on textile substrate. The electrolyte material used was a dispersion of polyethylene dioxythiophene: polystyrene sulphonate (PEDOT:PSS) from Ossila company. It was not easy to directly determine the energy stored in these devices, therefore the energy in the cell was estimated from the energy it supplied to the voltmeter. Using the equation relating energy to the capacitance, the capacity of the developed device was estimated to be 180µF.

The capacitor was charged normally and used to power a calculator. We stretched the capacitor and charged it at an arbitrary voltage of 3 V and roughly 40 minutes instead of the normal 1.5V for 2hrs. After charging the capacitor for sufficient time at 3 V, the accumulated charge in the device was about 1.2 V, but for a short time. In these experiments too, a sharp voltage drop was observed initially for a few seconds as it has been throughout the other experiments, then the voltage discharge slows down. Despite the self-discharge of the capacitor, a calculator (TOSHIBA LC-810) could run on the developed cell for 37 seconds.

This work is concluded by chapter 8 with a list of main achievements presented in this dissertation and recommendations for future work.

List of Abbreviations

EDLC	Electric double layer capacitor
MWCN	Multi wall carbon nanotube
SWCN	Single wall carbon nano tube
PAN	Poly acrylonitrile
PANI	Polyaniline
PBO	Polybenzoxazole
PEDOT	Polyethethylene dioxythiophene
PSS	polystyrene sulphonate
PEDOT: PSS	Polyethethylene dioxythiophene : polystyrene sulphonate
PPY	Polypyrrole
REDOX	Reduction/oxidation
TPU	Thermoplastic polyeurethane

Greek symbols

ρ	Resistivity
E_0	Electric field
E_{el}	Electric energy
η	Efficiency
ε_0	Permittivity of free space $8.8*10^{-12}$ F/m
ε_r	Dielectric constant or relative permittivity
ψ	Electric field strength
Ω	Ohm
$\boldsymbol{\phi}$	Potential distribution

Roman symbols

A	Area of electrodes measured in square metre (m^2) (dielectric)
C	Capacitance

d	Distance between the plates/ electrodes
$R_\square$	Square resistance
a	Distance between two electrodes

Units

%	Percentage
µWh	Microwatt hour
^{0}C	Degree Celsius
Ah	Ampere hour
F	Farad (electric charge unit)
F/g	Farad/ gram
g	Gram
J	Joule
KΩ	Kilo Ohm
m	Metre
mAh/g	Milliampere hour per gram
mJ	Milli Joule
MΩ	Mega Ohm
mV	Milli volt
nA	Nano ampere
R	Resistance
τ	Time constant
s	Second
t_{ini}	Initial time
V	Is the voltage at any point in the discharge curve
V_o	Initial voltage
W	Watt
W/kg	Watt per kilogram
Wh/kg	Watt hour per kilogram

List of Publications

A1 Publications:

- Odhiambo, S. A.; De Mey, G.; Hertleer C.; Schwarz, A.; and Van Langenhove L., "*Discharge characteristics of poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) textile batteries; comparison of silver coated yarn electrode devices and pure stainless steel filament yarn electrode devices*.“ Textile Research journal 2014 (84) 347-354.

- Odhiambo S. A.; Hertleer, C.; Van Langenhove L.; and De Mey, G. "*Reliability testing of PEDOT:PSS capacitors integrated into textile fabrics*." Maintenance and Reliability Journal 2014 (3) 440-445.

- Odhiambo S. A.; Hertleer, C.; Van Langenhove L.; and De Mey, G. *"Electric energy stored in PEDOT:PSS capacitors integrated into textile substrate: limits and possibilities*" (under review).

- Odhiambo S. A.; Hertleer, C.; Van Langenhove L.; and De Mey, G. *Influence of yarn electrode diameter on the discharge characteristics of PEDOT:PSS textile capacitors* (under review).

P1 Publications

- Odhiambo, S. A., De Mey, G., Hertleer, C., Fiszer, P., Napieralski, A. & Van Langenhove, L. `Use of Electric Energy Stored in a Textile-based PEDOT:PSS Capacitor´, *22nd International Conference on Mixed Design of Integrated Circuits and System* Torun - Poland MIXDES (2015).

- Odhiambo, S. A., Hertleer, C., Van Langenhove, L., De Mey, G., De Ferme, W., & Stryckers, J. ´Comparison of commercial brands of PEDOT: PSS in Electric "Capattery" integrated in textile structure´. *Mixed Design of Integrated Circuits and Systems, Proceedings* (pg. 389–391, Gdynia-Poland. MIXDES (2013).

C1 Publications

- Odhiambo S. A.; Hertleer, C.; Van Langenhove L.; and De Mey, G. 'Investigation of performance of different types of yarn electrodes in a PEDOT:PSS capacitor' *14TH World Textile Conference.* Congress center, Bursa - Turkey: AUTEX, (2014).

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- Odhiambo, S. A., Van Langenhove, L., De Mey, G., & Hertleer, C. (2013). Pedot: PSS based electric capacitors integrated on textile fabrics. *Techtextil- und Avantex Symposien, Abstracts* (pp. 1–24). Presented at the Techtextil- und Avantex Symposien, Messe Frankfurt
- Odhiambo, S. A.; Hertleer, C.; De Mey, G. and Van Langenhove, L., ‘Flexible batteries’ ***ArchIntex Network***. Ronse -Belgium, TIO3 textile incubation centre 2013
- Odhiambo, S. A., Hertleer, C., De Mey, G., & Van Langenhove, L. (2012). Possibilities of PEDOT: PSS electric capacitors integrated on textile fabrics. In G. Guxho (Ed.), *Konferenca V ndërkombëtare et tekstilit (abstraktet) = 5th International textile conference (abstracts)* (pp. 26–26). Presented at the 5th International Textile Conference, Tirana, Albania: Polytechnic University of Tirana. Faculty of Mechanical Engineering.
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- Odhiambo, S. A. “PEDOT:PSS capacitors integrated in textile fabrics”. 14th FEA symposium, Faculty of Engineering & Architecture, Ghent university Het pand (Ghent -Belgium) 2013.

A4 Publications

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- Hertleer, C., Odhiambo, S. A., & Van Langenhove, L. (2013). Protective clothing for firefighters and rescue workers. In RA Chapman (Ed.), *Smart textiles for protection* (Vol. 133, pg. 338–363). Oxford, UK: Woodhead.

1

General introduction

This chapter gives an overview of smart textile systems and focus on the energy storage unit as one of its major components. Conventional energy storage devices (batteries and capacitors), which are currently used as source of energy for smart textile systems will be discussed in detail in this chapter. Batteries are the main source of electric energy storage, however, capacitors could also be used in temporary storage. It is important to get an overview of both batteries and capacitors, in order to understand their similarities and differences. Current developments toward achieving flexible and comfortable textile batteries and textile capacitors will also be reported, including the challenges faced.

1.1 Smart textiles

Smart textiles are garments that in addition to normal body covering, can respond or interact or adapt to their environment. A smart textile system consist of sensors, actuators, connections, data processors, and antennae which are normally connected together as working unit.

Smart textile systems can be used in various applications, summarized as follows; see Figure 1.1.

Leisure and fun – future fashion, key boards, or flexible displays

Sports – Body activity, distance covered, speed, heart rate, heating or cooling functions.

Personal protective equipment – detection of external gases and temperature, and giving locations, heating or cooling garments.

Health and telemonitoring – electrocardiogram measurements, body activity, heart rate and body temperature.

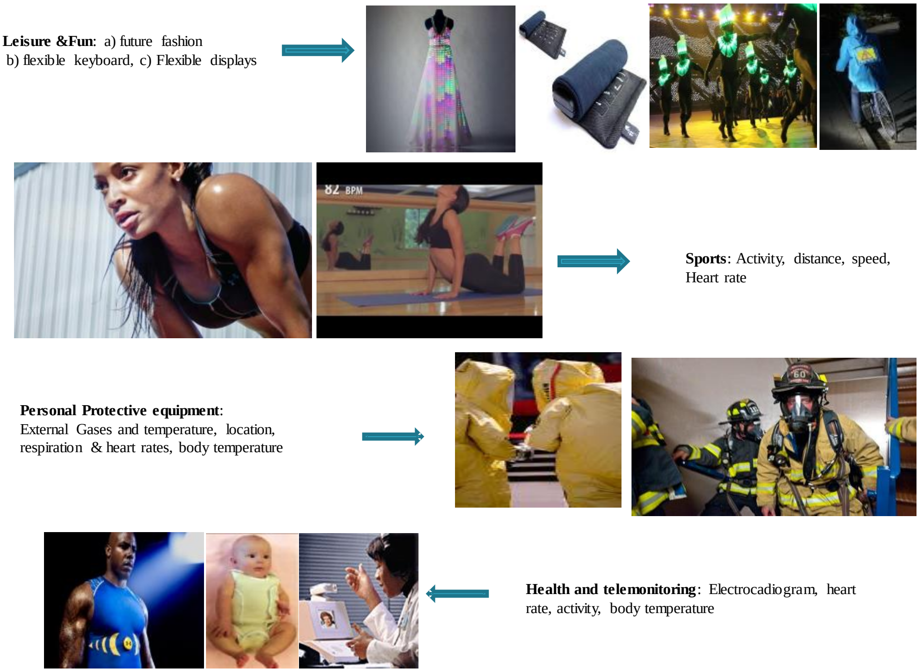


Figure 1.1 Smart textiles application areas

In most cases the smart textile system requires some source of energy to function. The energy supply can be from a stored energy source or energy generated on the spot. Energy stored in a device has the advantage that the smart system can be used throughout and wherever unlike in the case with the energy generating system where energy is supplied only after generation. This means if the generation mechanism is not enabled, the system will not work. For instance when using solar cells, as energy generators, it means, generation is possible only in the presence of sunlight.

The energy storage device needs to be light weight, flexible, comfortable and compatible with the garment.

1.2 Current situation of power storage for smart textile application

Existing prototypes of smart textiles come with rigid, bulky portable batteries that are placed in pockets within the garment. Sometimes the prototypes have to be plugged into an electric plug in order to operate. This limits the side spread usage of the garment and is not ideal to the users of the smart garments. This also does not provide comfort and ease of movement as compared to the textiles themselves. Flexible energy storage devices that are with fabric properties are non-existent. There is need to seamlessly integrate the various functional electronic components of smart textiles into textile matrices, at the same time maintaining the comfort of softness, flexibility and lightness of the textile material.

The energy storage device should be of light weight, flexible and have good drape properties. If possible it should be washable, to allow easy care of the textiles.

Research efforts are towards constructing a suitable energy storage device that is not bulky, light weight, flexible, reliable and well integrated within the textile material, that could be used comfortably in the various mentioned applications.

1.3 Batteries

Electric energy can be stored either in batteries or capacitors. Nowadays there are also power banks which are used to refill batteries. The energy storage devices are used with electronic systems to provide the required energy.

The smart textile system, which has electronic functionalities also requires some source of electric energy to provide power. The power can either be used from a stored source (battery) or generated as it is used (photovoltaic).

Batteries come in different sizes and shapes; cylindrical, button size and prism shapes. These conventional package shapes are as shown in Figure 1.2. However they don't suit well in some specific situations like in our smart textile system. Research is ongoing to develop function specific batteries like flexible, stretchable or miniaturized batteries.

Figure 1.2 Different sizes and shapes of batteries (cylindrical, prism and button batteries)

Current electronic systems combine a capacitor with a battery to boost the energy supply.

Electric energy can be stored in either capacitors or batteries. Capacitors have a quick charge-discharge rate (with high power delivery rate that lasts for a short time) while batteries have a slower charge - discharge rate with high power densities, hence can last for several hours. On the other hand, capacitors have longer cycle lives (limitless in ideal) than batteries.

There are different types of batteries, based on the material used to make the battery, for example lithium ion battery, nickel battery or zinc battery.

Research in conventional batteries is towards developing more efficient batteries that can provide required power for longer periods. The electrode materials, the cathode and the anode are key components that affect the energy density of the cell. For a good combination of selection of electrode material, the voltage work function between the anode and cathode should be large, (high potential cathode + low potential anode). So far Lithium ion battery electrode materials are of the highest potential with Li/Li^+ between 3.5 - 5V [1]. However the safety aspects of lithium ion batteries are debatable.

There are efforts also towards developing more thin, flexible batteries for phones and smart textile systems. Enfucell [2], and Blue Spark Technologies [3], are some of the companies that already produce thin flexible batteries. Also film cells exists and are manufactured already by companies like Ultra-life [4], into the materials. However, they still do not meet the current requirements for the smart textile system batteries. For smart textile applications the battery needs to be light weight, very flexible, comfortable and seamlessly integratable within the textiles. Therefore this research will address development of an energy storage device for smart textile systems, that is in line with these specifications

1.3.1 Classification of conventional batteries

Batteries are classified into *primary cells* which are meant for single use and *secondary cells* which are rechargeable and could be for multiple use. Recently, battery reserves have been developed, they are also known as power banks and are used to refill the secondary batteries.

Batteries are also classified according to the materials assembled to form the battery for example, lithium ion batteries, nickel cadmium or zinc batteries.

Batteries can also be classified according to the state of matter of the electrolyte material used, therefore there are dry cells, wet cells, or jelly cells.

1.3.2 Construction and working principle of a battery

A battery is normally composed of *electrodes* – (anode & cathode), an *electrolyte,* a *separator* and current collectors as the main components. Additionally they have binding material, container, terminals and seals as shown in Figure 1.3. The main components affecting the energy density of the battery are the battery electrodes; *cathode* and *anode.*

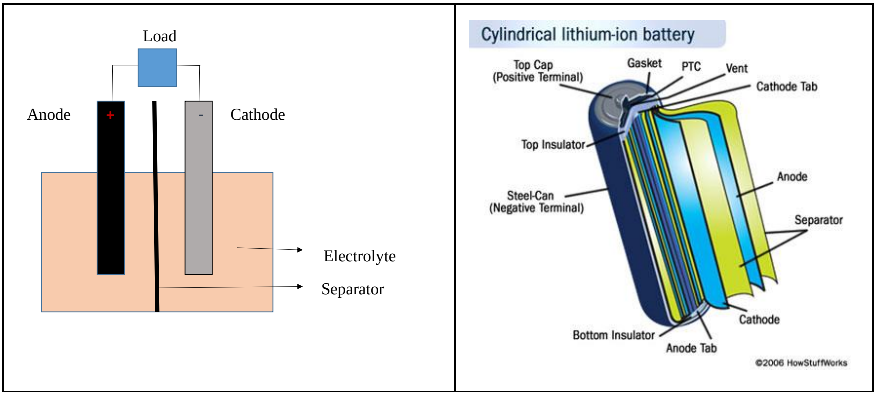


Figure 1.3 Basic components of a battery in their assembly

1.3.2.1 Electrodes

The electrical properties and ***energy densities*** of energy storage device are determined by the selection of electrode material.

Anode is the positive electrode that is normally oxidized i.e. loses electrons in a chemical reaction within the cell. An anode should be an efficient reducing agent with good conductivity. Metallic material such as zinc, nickel and lithium are often used as anode materials.

Cathode is the negative electrode normally a metal oxide or sulfide that is reduced or gain electrons. The main properties of a cathode material is that it should be an efficient oxidizing agent and should be stable when it comes into contact with electrolyte.

1.3.2.2 Electrolyte

Electrolyte: the medium which provides the ion transport mechanism between the positive and the negative electrodes. The choice of electrolyte is very important for the choice of electrode material [5]. Electrolyte in a battery perspective is a conducting medium that allows ion transport within the cell. External flow of electric current from the cell is initiated by migration of ions inside the electrolyte. Electrolytes are mostly in solutions with dissolved salts, acid or alkalis which are good for ionic conduction. The dissolved elements dissociate to give positive and negative ions which eventually give the electric current if connected to electrodes.

However, in solid electrolytes the phenomena is slightly different. Solid electrolytes allow movement of ions without the need of a liquid, the principle is based on hopping of ions within the solid structure. Electrolyte in supercapacitor perspective is more of ionic substance.

An ideal electrolyte should have high ionic conductivity and should be resistant to temperature fluctuations (sometimes the chemical reactions inside the cell produce heat). For example inherent instabilities of lithium metal, in lithium batteries especially during charging. The temperature would quickly rise to the melting point of the metallic lithium and cause a violent reaction. A large quantity of rechargeable lithium batteries had to be recalled in 1991 after the pack in a cellular phone released hot gases and inflicted burns to a man's face [6].

1.3.2.3 Separators

A battery separator is an ion permeable material that is electronically nonconductive. It is a spacer material which prevents electrical contact between the electrodes of opposite polarity in the same cell.

1.3.3 Charge - discharge of a battery

Conventional batteries store energy in chemical bonds. The chemical reactions (REDOX) produce ions that move from one electrode to the other. Each reaction in a battery is associated with a specific potential. The overall potential of the cell is the summation of these specific potentials. An electrochemical impedance measurement would give the specific potential of one electrode. This is evaluated by examining the interface of the active electrode against electrolyte. A voltage across the battery measures the energy difference between the positive and the negative electrodes.

In order to charge a battery, it must be subjected to potentials/voltages higher than its existing voltages or intended voltages for a newly assembled battery. In the charging process as indicated in Figure 1.4 anions flow to the cathode, cations flow to the anode. A reduction process takes place at the anode while oxidation is at the cathode. Charging reverses the chemical reaction that took place in the discharge process. The higher the voltage, the faster the charging rate but this is subject to some limitations.

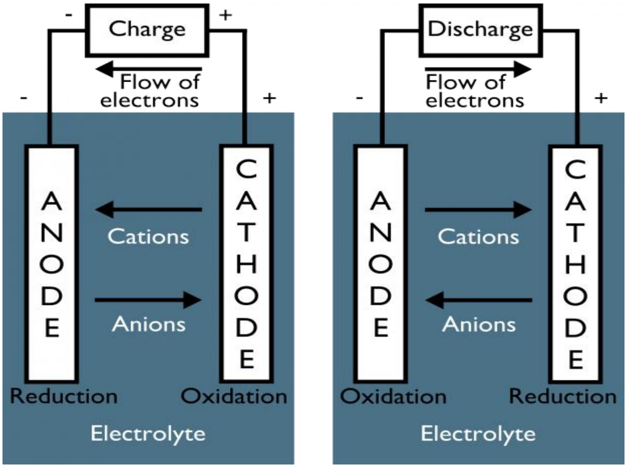


Figure 1.4 Charge-discharge of a battery

1.3.4 Power ratings of a battery

The main physical properties one should care about a battery are ***the energy*** it can give, ***its power***, ***mass and volume***.

Batteries are rated according to their voltage and capacity in terms of the hours they can give a specific current to a load, say 9V, 20mA for 16 hours.

Battery capacity can be expressed in terms of energy (J) or power (W).

Energy is measured in Joule (J), the relationship between energy and power is given in Equation 1 and Equation 2.

$$\boldsymbol{Power\ in\ watt}\ (\mathbf{W}) = \frac{\mathbf{Energy\ (J)}}{\mathbf{Time\ (s)}}$$ **Equation 1**

Therefore

$$\mathbf{1\ Wh = 3600\ J}$$ **Equation 2**

Energy density is energy per unit volume or energy per unit mass. Energy per unit mass is also known as specific energy measured in (Wh/kg).

Power density is power per unit mass (W/kg).

Capacity is the measure of the amount of electric charge in coulomb (C), however, in battery literature ampere-hours (Ah) is often used instead of coulomb, see Equation 3.

$$\mathbf{1\ Ah = 3600\ C;\ and} \qquad \mathbf{Volt\ (V)} = \frac{\mathbf{Joule\ (J)}}{\mathbf{Coulomb\ (C)}}$$ **Equation 3**

A battery in a laptop of 3Ah can deliver 3 amperes for a period of 1 hour or 1 ampere for 3 hours. With an output voltage of 10V, maximum amount of energy in this battery is 10V X 3A X 1h = 30Wh = 0.03kWh = 108000Joules.

1.4 Capacitors

A capacitor is an energy storage device that stores energy electrostatically in an electrostatic field. They have high power densities with low energy density, therefore they can give high power in a short time There are three classification of capacitors: *electrostatic capacitors* Figure 1.5, *electrolytic capacitors* Figure 1.6, and *supercapacitors* Figure 1.7. In terms of shape, conventional capacitors also come in various sizes and shapes like the batteries: cylindrical, button size and prism.

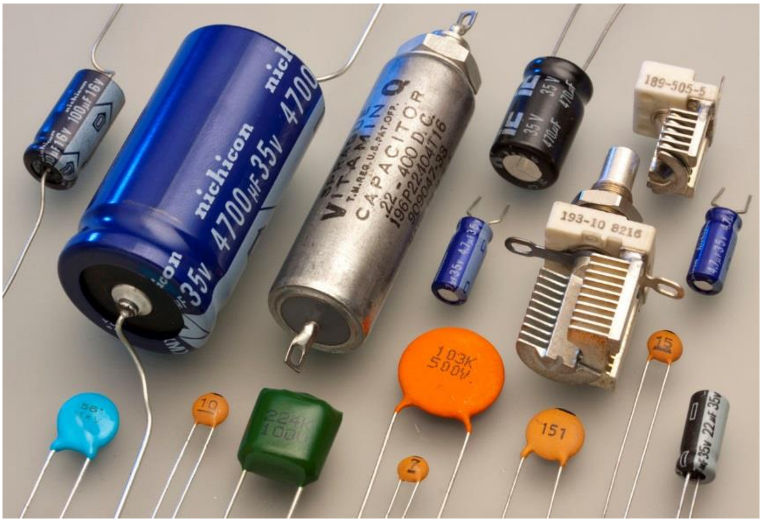


Figure 1.5 Different sizes of electrostatic capacitors

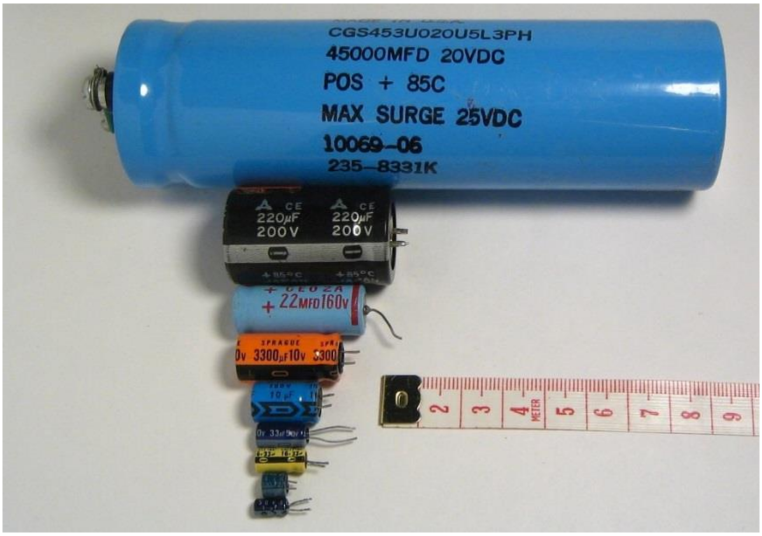


Figure 1.6 Different sizes and shapes of electrolytic capacitors

Figure 1.7 Different sizes and shapes of supercapacitors

1.4.1 *Classification of capacitors*

The main types of capacitors as already stated are the *electrostatic, electrolytic* and *supercapacitor*, the capacitor´s internal designs are presented in Figure 1.8. An electrostatic capacitors has a dielectric material in between the two electrodes. Electrolytic capacitors has an ionic liquid or electrolyte that forms a metal oxide with one of the electrodes. This oxide layer is also denoted as dielectric in Figure 1.8. Supercapacitors have electrolyte in between the electrodes. Therefore the basic components of capacitors are the electrodes (plates) and electrolyte or dielectric material. Sometimes a separator is needed to electrically isolate the two oppositely charged electrodes. The electrodes are normally attached to a current collector.

Supercapacitors are further classified into non-Faradaic (electric double layer capacitors(EDLC)) and Faradaic (pseudocapacitors) as shown on the right side of Figure 1.8. This division is based on the charge storage principle. The charge storage in electric double layer is purely by separation of charges within the electrolyte that are then accumulated on the electrodes. However in Pseudo capacitors charge storage is through a charge transfer from the REDOX reaction.

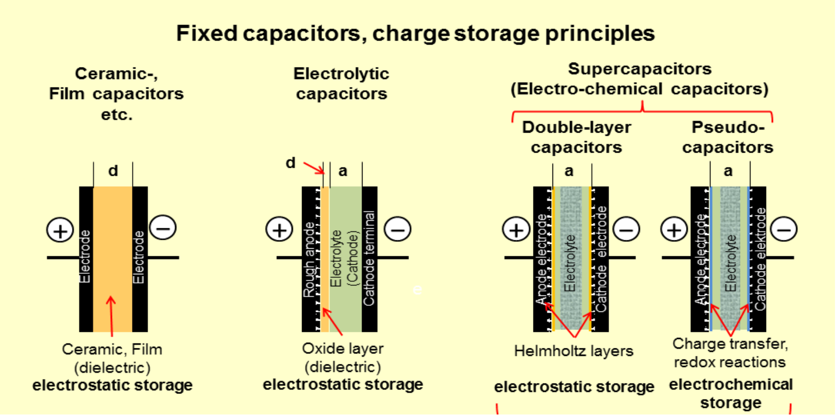


Figure 1.8 Types of capacitors. Source: [7-10]

An electrostatic capacitor is composed of two conductive plates of the same material, separated by a dielectric material. These capacitors store energy in an electrostatic field and are typically with a dielectric material in between the electrodes, which is a dry separator as shown in ceramic film capacitors in Figure 1.8. They have low capacitance in the range of pico-farad to low microfarad, and are used in tuning radios and filtering signals.

Electrolytic capacitors use an electrolyte or ionic conducting liquid as one of their electrodes. One of the electrodes has an oxide layer which has been referred to as the dielectric. The capacity of this capacitor is several thousand times that of an electrostatic capacitor. They are used in power filtering, buffering and coupling.

Supercapacitors have very high energy density, thousands of times higher than electrolytic capacitors [5, 8, 11]. They are applied in electric vehicles, electric hybrid vehicles, mobile phones, digital cameras and uninterruptible power supplies among others [12-15].

Supercapacitors are further subdivided into two according to their operation principles. Electric double layer capacitors store electrical energy in electrostatic field while the pseudo capacitor store charge via reversible fast redox reactions [10]. The electrode material of supercapacitors are of high specific surface area and of good conductivity. The electrode materials used in supercapacitors are either *carbon based material* or *conducting polymers (polyaniline and polythiophenes)* or *metal oxides* such as cobalt or manganese oxide [12, 16, 17].

1) *Electric double layer capacitors* (EDLC) in which the electrode material is not electrochemically active, see to the left of Figure 1.9, charge storage is by pure physical charge accumulation [8, 11] at the electrode/electrolyte interface. The capacitance of an EDLC is associated with an electrode potential dependent accumulation of static charge at the interface.

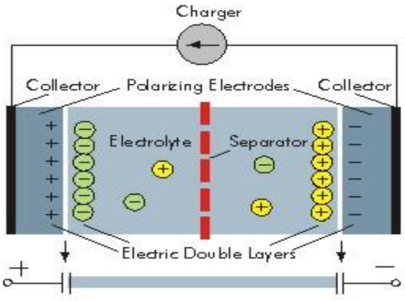


Figure 1.9 Electric double layer capacitor

2) *Faradaic/Electrochemical supercapacitor* or *pseudocapacitor* [5, 10, 18] is one in which the electrode material is chemically active, the electrochemical process occurs both on the surface and in the bulk near the surface of the solid electrode. When a potential is applied to this capacitor first and reversible faradaic reactions (REDOX) take place on the electrode material, similar to

the process that occurs in batteries see Figure 1.10. Faradaic supercapacitors have much larger capacitance values (10-100 times) and energy densities than EDLCs. Example of material used on the electrodes is a metal oxide in combination with carbon based material (collector). Working voltage depends on the decomposition of the electrolyte. An electrochemical supercapacitor (pseudocapacitor) is not a battery per se but crosses the boundaries into battery technology since it uses specialised electrodes and electrolytes. A hybrid electrochemical capacitor that one electrode is an electrostatic carbon material and the other electrode is of faradaic capacitance material are being studied and developed to capitalize on the electrode materials advantages and improve overall performance of the device in terms of cell voltage, energy and power densities.

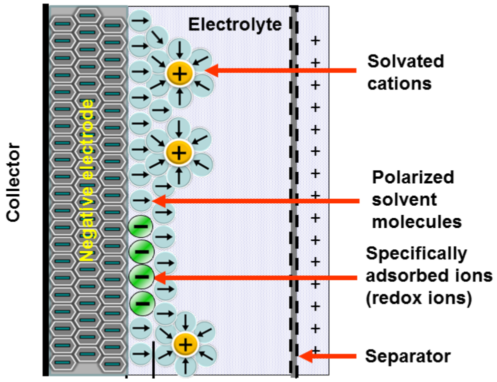


Figure 1.10 Electrochemical action on the surface of the negative electrode of an electrochemical cell

Electrically conducting polymers such as polyaniline (PANI), polypyrrole (PPY) and polyethylene dioxythiophene (PEDOT) have been used as materials for cathode in electrochemical capacitors (positive electrode) [19] while carbon based graphene and carbon nanotubes are used as the anodes (negative electrode) [20]. The conducting polymers have been considered in this application because of their excellent capacity for energy storage, conductivity and low cost, however, their stability is questionable due to their swelling and shrinking which leads to degradation of electrodes during cycling. The polymers have different degrees of stability. PEDOT is the most preferred in terms of stability. When electro conductive polymers are deposited as thin coating on supporting substrates such as clothing or paper, they give high energy and power densities [19, 21]. Oxidation - reduction reactions in conjugated polymers are normally followed by transportation of the charged particles, the ions and the electrons. It is also associated with volume change in the conjugated polymers.

Supercapacitors made from conductive polymers are classified into three categories. To understand these classification of polymer based supercapacitors we need to describe doping. Doping refers to introducing small quantities of elements (impurities) to semiconductor molecules that change their electrical conductivity by either generating surplus valence electrons or creating a deficiency in valance electrons. There are two types of dopant (impurities); n-type and p-type. N-type dopants act like electron donor while p-type dopants act as electron acceptor.

Conductive polymer based supercapacitors are classified as:

- *Type I* (symmetric*)* in which both the electrodes use the same p-dopable polymer. In fully charged state the positive electrode is fully p-doped while the negative electrode is in uncharged state.
- *Type II* (asymmetric*)* two different p-dopable conductive polymers are used for the electrodes such as polypyrrole and polythiophene.
- *Type III* (symmetric), these supercapacitors are of the n-p type. Electrodes use same material which can both be p- and n- doped in the same molecule [8, 18]. The performance of the prepared electrode must be evaluated in real supercapacitors of two cell electrodes [22]

Supercapacitors are of special interest of late and are also targeted for use in electric vehicles and railway electrification where they supplement batteries in the systems.

1.4.2 Energy stored in a capacitor

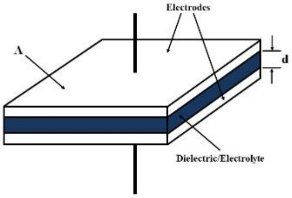


Figure 1.11 Conventional electrostatic capacitor

The energy stored in a capacitor can be calculated from its capacitance using presented Equation 4.

$$E = \frac{1}{2}QV = \frac{1}{2}CV^2$$ **Equation 4**

Where E: energy

V: voltage

Q: charge

C capacitance.

The capacitance in turn is obtained from the parameters of the capacitor using Equation 5

$$\boldsymbol{C = \mathcal{E}_0 \mathcal{E}r \frac{A}{d}}$$ **Equation 5**

where

C : capacitance in farad (F)

A : area of electrodes measured in square metre (m^2)

ε_0: permittivity of free space $8.8*10^{-12}$ F/m

ε_r : dielectric constant or relative permittivity of the material in between (dielectric)

d : distance between the plates

The energy stored in the capacitor is inversely proportional to the distance between the plates/electrodes. The specific energy of a capacitor would be given per the weight of the electrodes, and is measured in Farad per gram (F/g) of electrode material. Therefore the type of material and construction of the electrodes is important in a capacitor. The specific energy of the capacitor is given in Wh/kg.

1.4.1 Charge – discharge of a capacitor

Capacitors store charge by means of static charges except the pseudo capacitors. The capacitor is charged by applying a voltage over it for a short time.

An ideal cycle of charge - discharge of a capacitor is shown in Figure 1.12. The capacitor takes a short time to charge to the maximum level of voltage in the charging phase. In the discharging phase, the voltage decays exponentially. A capacitor stores charge, and the voltage across it is proportional to the charge stored. The exponential voltage decay is given by Equation 6:

$$\boldsymbol{V = V_0\, e^{-t/\tau}}$$ **Equation 6**

Where

V is the voltage at any point in the discharge curve

V_o is the initial voltage

R is resistance

C is capacitance

Tau (τ) = RC= time constant of the exponential decay.

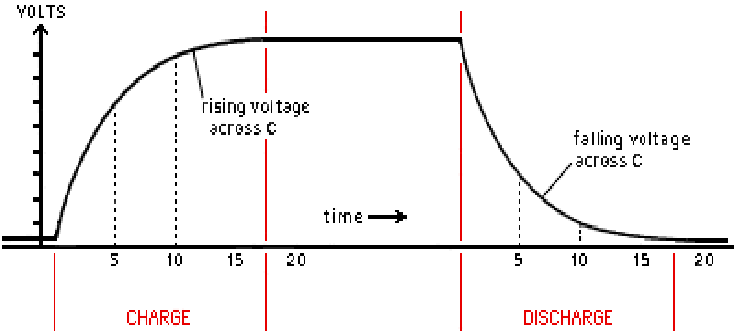


Figure 1.12 Charge discharge cycle of a capacitor Source [23]

A hybrid capacitor in terms of energy storage mechanism also exists. Hybrid systems combine a battery like electrode and capacitor like electrode for energy source and for power source respectively in the same cell. It should be noted that originally electrochemical reactions belong to the batteries and capacitors are known not to have any chemical reactions, apart from the recent developments in pseudocapacitor, and this is the main difference between a battery and a capacitor.

1.5 Batteries versus capacitors

The similarity between a battery and a capacitor is the fact that they have similar structural components; the electrodes and the electrolyte. Also the energy-giving process takes place at the electrode/electrolyte interface; in capacitors, the energy is in form of accumulated charges, while for electrochemical cells there is a REDOX reaction at the electrode/electrolyte interface.

The main difference is that there are no chemical reactions in capacitors except for pseudo capacitors, while in batteries there are chemical reactions. This aspect is responsible for the fact that you can charge a capacitor in a short time, and discharge it in a short time too, while a battery needs longer time to charge – discharge as shown in Figure 1.13. Batteries have a huge storage capacity, but because of the chemistry involved electricity can go in and out only so fast, and some (typically 10-40%) is lost as heat in the chemical reactions. Normally the absence of chemical reaction in capacitors is a big advantage in their cycle ability (charge-discharge) which is ideally unlimited and the energy can be given quickly in large quantities. They can be charged in minutes or seconds, they deliver energy quickly and with unlimited life cycle.

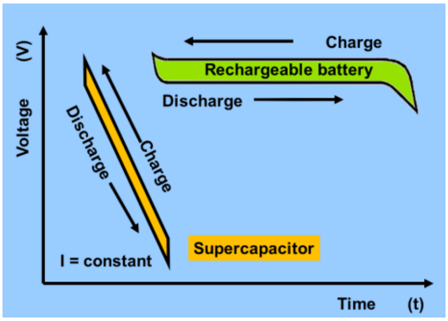


Figure 1.13 Comparison of charge discharge graphs of a battery vs a capacitor (Source [24])

Since the lithium ion batteries are the most commonly used as source of energy storage in smart textile applications, its parameters will be compared to those of a normal capacitor and a supercapacitor. The comparison is given in Table 1.1.

Table 1.1 Parametric comparison of various forms of energy storage

Parameter	Lithium ion batteries	Capacitors	Supercapacitors
Energy density (Wh/kg)	100 - 265	0.01 – 0.03	1.5 – 9.0
Power density (kW/kg)	0.3 – 1.5	>100	2 -10
Charge – discharge cycles	500 - 10^4	unlimited	10^5 - 10^6
Self-discharge time at room temperature	Month(s)	Days	Week(s)

A clear pictorial comparison of power density against energy density of the various energy storage devices is shown in Ragone plot as Figure 1.14.

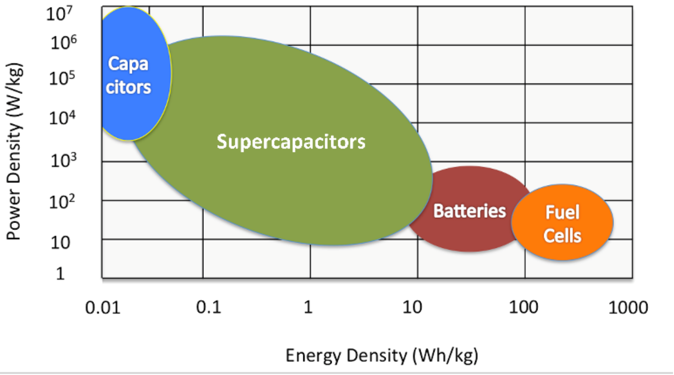


Figure 1.14 Ragone plot: power density Vs energy density of various energy storage devices Source:[9]

From the Ragone plot we clearly see that normal capacitors have high power densities with low energy densities while the batteries have low power densities with high energy densities. Energy storage devices that have fast charge - discharge rates (high power delivery rate), high power densities and have long cycle lives [11] are very promising in powering next generation mobiles, electronics and smart textile systems.

1.6 Background of textile-based batteries and capacitors

The term textile-based implies that a textile process, textile technology or textile material is used in fabricating the energy storage device in question. With a clear knowledge of conventional energy storage devices it would be good to appreciate the effort made by a handful of researchers working in this area. All the researchers have an aim of integrating energy storage devices seamlessly into yarns or fabrics so that they are part of the textiles and can be used with smart textile systems, instead of using detachable energy storage devices which are non-flexible components. Limitations of the current energy storage devices have been presented in Section 1.2.

1.6.1 Flexible textile-based batteries

A lot of research is on-going to make a flexible textile battery. The main aim is to produce a functional battery that is either directly incorporated in the fabric [25, 26], or yarn [27-30] itself which is eventually woven into a fabric. The battery is expected to be light, flexible and comfortable to the user. At fabric level, the battery is achieved by assembling the battery components (anode, cathode, separators and electrolyte) as separate yarns assembled together to form a battery unit or as pieces of fabrics that are laminated together by various technologies. When the battery components are in the form of yarns, they are converted into batteries by either of the conventional textile technologies, i.e. weaving [25] or knitting [26].

The challenge is to identify cheap materials which can easily be combined to make the battery. The most common used technology in research to incorporate a battery into fabric is weaving. Battery yarns are inserted into fabric using the weaving process as weft yarns with less stress on the yarns.

Printing [31, 32] technology is also used, where either of the battery components are printed on the fabric in layers. In some cases a combination of weaving/knitting and then printing is applied [31]. Another technology involved that was used recently in producing a battery on any surface is painting technology [33].

At yarn level, all the battery components are assembled in a yarn, cable, tape or stripe which can be woven [28-30] or different battery components are presented by yarns which are assembled by weaving to form the battery [34].

A battery spool has been produced by fiber drawing technique [35], copper and aluminium wires were inserted in a fiber preform made from polyethylene, but shaped inside to contain electrolyte. These were assembled in a continuous process and heat set, like in the fiber drawing process.

Fiber batteries have been produced by sequentially depositing thin layers of battery components (anode, electrolyte, cathode) by vacuum deposition technique, including magnetron sputtering and electron beam evaporation [36]. The advantage of these power fibers is their inherently large surface area, for example, a thin-film battery fabricated on a 50 micrometre thick foil substrate of 1 cm x 1 cm area has a maximum available battery area of 2 cm^2 (double-sided fabrication) compared to 6.28 cm^2 of two layers of 25 micrometre thick power fibers of 1 cm length.

Liu *et al.* [25] made strips of thin lithium batteries with solid electrolyte which are woven into a fabric. The battery strips are woven into the textile as weft yarns while the majority of warp yarns are maintained as the textile material. A number of conductive yarns included in the warp yarns are used to connect the battery stripes into series.

Hu *et al.* [26] produced a lithium ion textile battery in which they wove a conductive porous 3D structure from conductive yarns made of pure polyester dispersed with carbon nanotubes. These are then filled with battery electrode material and electrolyte. The assembly is then stuck on a flat metallic piece which is the current collector.

Bhattacharya *et al.* [37] produced a textile battery based on a jacquard woven fabric as textile substrate. The textile base is woven with inclusion of three silver coated polyamide yarns (electrodes), which are placed very close to each other approximately 1mm apart according to the weaving pattern. PEDOT:PSS from H.C. Starck [38] is then systematically drop coated on the substrate at a defined small area within the conductive yarns (see Figure 1.15). The PEDOT:PSS is normally spin coated onto a planar surface in order to give a uniform coating, however, given the open structure of textile, spin coating was not possible. The coating process was done at an ambient temperature of 90^0C – 100^0C.

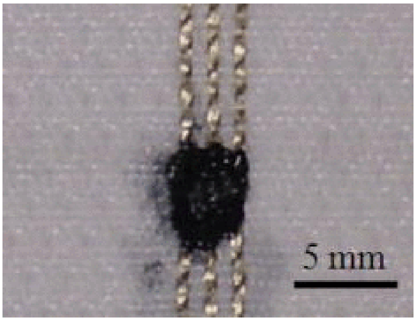


Figure 1.15 PEDOT based charge storage device on a textile substrate

Multiple coatings of PEDOT:PSS were applied over each previous coat in order to decrease the bulk resistance. In total, seven coats were used in the fabrication process, with each coat consisting of 0.5 ml of PEDOT:PSS uniformly deposited over a 60mm^2 area. Before application of a new coat, the sample was allowed to cure in an oven at 90^0C – 100^0C for 15 min. As much as the PEDOT:PSS was applied carefully in a uniform manner onto the textile substrate, the final film had an uneven surface morphology.

Just after fabrication the device was found to have no measureable stored charge and an open circuit voltage of 0V. After cyclic voltammetry, the sample was found to have a short circuit current of 30 nA and an open circuit voltage of 50 mV. They discovered that the device could be recharged. After each of the recharging period, the bias was removed and the discharge current measured for a period of 2000s. After each recharging period a metallic colour was observed forming on the PEDOT surface. Using scanning electron microscope (SEM) imaging and energy dispersive X-ray (EDAX) it was determined that the metallic colour came from formation of silver crystals, very small amounts of oxygen and sulphur were observable in the formed silver crystals, indicating that they were metallic silver and not silver oxide or silver sulfide. Figure 1.16, shows the current against time discharge characteristics of PEDOT coatings, between each discharge period the device is recharged for 1000 s at 1.5V.

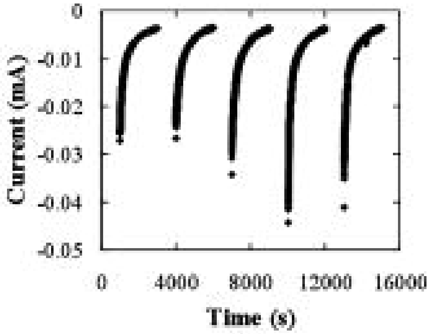


Figure 1.16 Current against time of charge - discharge characteristics of the PEDOT coatings on silver coated yarn electrodes

Bhattacharya *et al.* [37] claim to observe larger concentrations of silver on the cathode and not on the anode in the first recharging period. The amount of silver increased on the cathode with each subsequent recharge, implying that the PEDOT acted as an electrolyte that silver can migrate through in the presence of an electric field. The metallic silver movement present in the PEDOT layer is consistent with the expected chemical interaction at the Ag/PEDOT interface shown in other research works. It has been shown that silver and silver compounds in contact with PEDOT will diffuse as silver ions into PEDOT via charge and mass transfer processes [39-41], “When a high electric field is applied to the PEDOT, the silver ions will diffuse through the PEDOT, from the anode to the cathode and recombine with electrons to become mostly silver metal”[42]. “When the PEDOT is biased, the region around the anode is oxidized (doped further with holes) and the region around the anode becomes reduced (de-doped with electrons), at the same time silver ions migrate some distance into PEDOT film.

When the potential is released electrons from the reduced region will recombine with the holes from the doped region as well as silver ions in the PEDOT matrix” [40, 41, 43]. In summary, Bhattacharya *et al.* [37] designed a rechargeable charge storage device on a textile substrate by applying a conductive polymeric coating (PEDOT:PSS) over interwoven conductive yarns (silver coated yarns).

1.6.2 Flexible textile-based capacitors

Many researchers are working in the direction of obtaining a flexible textile-based electrochemical capacitor for emerging new applications like smart textiles. Just like in batteries, efforts are also towards making flexible supercapacitors, either on fibers/yarns [31, 44-47] or on fabric.

These supercapacitors use modified conventional textile material as either the base material where thin active layers of electrodes and electrolyte are applied on, or as the main active component, say the electrode or the separator or the carrier within the supercapacitor. If the textile material is used as the base, it is normally modified by adding conductive polymers or metal particles to it by various techniques (coating, printing, deposition, dispersion, on site polymerization, etc.).

The combination of highly porous conductive carbon nanotubes, conducting polymers or metal oxides with textiles to maximize on the supercapacitor electrodes functionality has been researched on. For example, a flexible supercapacitor textile electrode was made from a conductive cotton textile sheet that was produced by dipping the cotton material several times in MWCNT (Multiwall Carbon Nanotubes) (to increase the MWCNT loading on the fabric) [48]. Pseodocapacitive cobalt hydroxide is then well dispersed into the conductive cotton textile sheet that it gives a large area specific capacitance of 11.22 F/cm^2 [48]. The composite delivers large area specific capacitance of 11.22 F/cm^2 and good electrochemical stability, with capacity loss of 4% only after 2000 cycles. Cyclic voltammetry and electrochemical impedance spectroscopy experiments showed that this composite has a good electrochemical capacitive nature. The material assembled in this composite binds together thus the need of binders or conducting additives is eliminated [48].

Remarkable success has been achieved by producing energy storage devices through incorporating Single Walled Carbon Nanotubes (SWCN) into textiles, and also using graphite electrodes [26, 49]. However, these compounds are not very safe to the human health and to the environment. Flexible and stretchable film batteries have been made using lithium battery materials and woven with the yarns to make batteries for smart textile applications [25].

In other scenario the textile substrate can be used as a separator and/or the dielectric material or carrier of electrolyte. The electrodes are then applied on both sides of the textiles. A combination of either of the three functionalities of the textile material in supercapacitors assembly can also be achieved.

Flexible supercapacitors were made from PEDOT nanofibres and PAN nanofibres by Larfogue *et al*. [50]. The PEDOT nanofibres were produced by combination of electro-spinning and vapor-phase polymerization, and were used as the active material (electrodes), separated by a sheet of PAN nanofibres. Carbon-based clothes were used as the current collectors.

Flexible supercapacitors were also made from carbon fibers by Shi *et al,* [51]. They prepared flexible electrodes in different ways mainly to have the conductive carbon network within them.

Fiber drawing method was also used to produce soft fiber supercapacitors [52]. They are prepared by first rolling and stacking conductive and dielectric films into a multilayer preform structure. The preform is then heated to a temperature close to the glass transition temperature, and finally drawn by a fiber tower at temperatures above glass transition.

1.6.3 Deductions

This chapter has given a wide overview of electric energy storage devices (batteries and capacitors), and the research efforts made towards achieving flexible textile-based batteries and capacitors. However a functional, fully integrated energy storage device is yet to be developed.

In this dissertation we identify with the work of Bhattacharya *et a*l. [37], which has been discussed in detail in section 1.6.1. We developed a similar charge storage device, in a simplified way but with different types of yarn electrodes. We obtained new findings which have been reported in our publications [53, 54]. We used Bhattacharya *et al.* [37] research as the basis and came up with a cheaply produced, comfortable, flexible and light weight energy storage device that is better in performance compared to theirs.

In subsequent chapters we discuss the materials used in the fabrication of our developed charge storage devices, the fabrication process, the charge – discharge procedures and results in terms of the performances of the developed devices and the controversial issues.

2

Materials used and cell fabrication

This chapter discusses the materials used to make the cell or the charge storage devices. The challenge was to find alternative materials for making an electric energy storage device well incorporated into textiles without affecting the textile properties. It is well known that most conventional commercial energy storage devices are made from chemically strong materials that need to be packaged in hard and compact casing, to contain the battery components and to prevent exposure to users and to the environment because of their toxicity. However, the hard casings make the energy storage devices solid, heavy, non-flexible and not comfortable to the wearer when used with smart textile systems. Additionally, a lot of safety guides are needed in disposal of the conventional battery after use. Therefore to come up with a textile compliant energy storage device, we opt for safer alternative materials, that could be assembled together.

The aim of this research is to make a flexible textile-based energy storage device from textile materials. The cell is expected to be light, flexible and part and parcel of the garment, with all the comfort of wearability. The term cell and charge storage devices will be used interchangeably.

2.1 Introduction

In this work, different types of materials: different types of yarn ***electrodes*** and one type of ***electrolyte*** with possibility to make an energy storage device were studied. Yarn electrode materials were readily available in the department, the electrolyte was purchased. These materials could interact together in a specific assembly according to the Bhattacharya *et al.* [37] design, to emulate the simplified configuration of an energy storage device. The assembly was also expected to function as a conventional battery. The basic structural components of a battery are electrodes (anode and cathode), electrolyte, current collectors and separator.

The casing was not considered in our design. However, it is also an important part of the battery but does not contribute much to the energy density of the cell. If anything most casing are the result of non-flexible batteries however, they are needed to contain the elements in a compact way and to protect us against the environment. The materials used in this research to assemble the charge storage device are discussed under the topics of *electrode materials*, *electrolyte* and *textile substrates* as separator and holder of the whole device.

2.2 Electrolyte

Since we aimed at having the device on a fabric without covering, a non-liquid electrolyte was preferred. We selected one of the intrinsically conductive polymers as our electrolyte since it has proven electrolyte properties [37]. This intrinsically conductive polymer is polyethylene dioxythiophene: polystyrene sulphonate (PEDOT:PSS), a mixture of two polymers.

Different types of PEDOT:PSS were used as electrolyte. The commercial brands of the polymer used were:

2.2.1 Drop coated

PEDOT 4083 (spin coat) from OSSILA [55]

ORGACON^{TM} ICP 1050 (spin coat) from Agfa [56]

Clevious P VP AI 4083 (spin coat) from Heraeus [57]

2.2.2 Screen printed

Clevious SV3 (printable) from Heraeus [57]

Clevious SV4 (printable) from Heraeus[57]

As a starting point, we chose PEDOT:PSS from Ossila randomly. We later found out that there were many different types of PEDOT:PSS which we also experimented as described in Chapter 5. However, they did not give good results. Note that these are not the only types of PEDOT:PSS available in the market.

PEDOT:PSS was used as a solid electrolyte in our cell making process. The dispersion was applied to the fabric in layers by drop coating technique and also by screen printing to form a dried layer of electrolyte coating.

There was need to evaluate the different types of PEDOT:PSS electrolyte in our device, and settle for the best brand in terms of easy application technology and reproducibility. However, the different types of PEDOT:PSS behaved differently in our devices, where we later discovered the wide range of behaviour of this polymer.

A brief discussion on the conductive polymers especially PEDOT:PSS will be given in the following section 2.3, to demonstrate their unique aspects that make them qualify for the electronic applications and the difficulty faced in studying their behaviour in the developed devices.

2.3 Conductive polymers

The main intrinsically conductive polymers well known are polythiophene, polyaniline and polypyrrole. Derivatives of these conductive polymers are employed in the development of different types of organic electronic devices including energy storage devices. The products from the organic conducting polymers are environmental friendly, light weight, flexible and adapt to the current requirements for textiles.

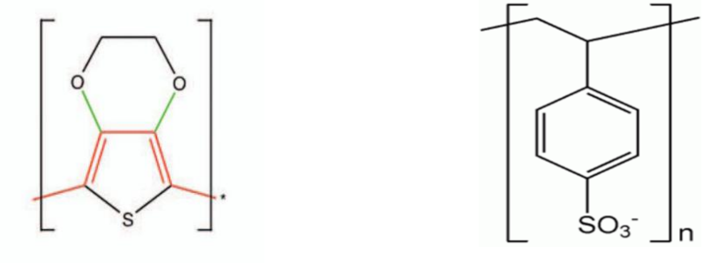
As much as we chose a conductive polymer as an electrolyte, in literature their application is mostly in electrode material of supercapacitors. Polythiophene and polyaniline derivatives are being researched on to develop new versatile, flexible and porous electrode materials for batteries and super capacitors [58]. The porous electrodes provide a high surface area, which enables huge amounts of energy to be stored in small volumes. These conductive materials have high theoretical capacities in the range of 100-140 mAh/g [59]. They are envisaged to produce energy storage devices which are flexible, lightweight and environmental friendly. However the capacitors from the conductive polymers have a problem with self-discharging and have poor long term stability. Different improvement technologies are being studied and employed, including using particular types of dopants which influence their electrical properties and stability.

2.4 Polyethylene Dioxythiophene (PEDOT)

PEDOT is a conductive polymer from the polythiophene family. Conductivity properties of PEDOT can be controlled at molecular level by using different types of dopants like PSS. The electrochemical properties of this conductive polymer depends on the size and mobility of the dopant element. PEDOT is of interest in most electronic applications because it is both p- and n-dopable [60]. PEDOT can transport either holes or electrons like in photovoltaic cells.

PEDOT in itself is not soluble in water, its solubility is circumvented by combining it with dopants like polystyrene sulphonate (PSS). It exhibits high environmental stability compared to polypyrole and polyaniline. Sustained heating of PEDOT at 150^0C under atmospheric conditions causes irreversible structural changes in its main chain [61]. Heating it to 200^0C increases the crystallinity.

The chemical structure of PEDOT & PSS is shown in Figure 2.1.



PEDOT

A

PSS

B

Figure 2.1 Chemical structure of (A) polyethylene dioxythiophene (PEDOT), & (B) of polystyrene sulphonate (PSS)

2.5 Polyethylene dioxythiophene: Polystyrene sulphonate (PEDOT:PSS)

PEDOT:PSS has gained a lot of popularity due to its wide range of conductivity, hence it has gained application in different areas in organic electronics. For example it is used to make flexible electrodes for various applications, used as buffer layers in organic light emitting diodes (OLED) as hole injecting and transporting material [62]. It has also got application in electronic displays [63], computer memory elements [64], electronic circuits [65], supercapacitors [50, 66, 67] and transistors [68].

PEDOT:PSS has been used as an electrolyte by some researchers to fabricate a rechargeable textile battery [37].

To obtain PEDOT:PSS, the polystyrene sulphonate (PSS) group is copolymerized with EDOTs in different proportions. The ratios of the PEDOT to PSS is varied by the manufacturers, depending on the targeted application. The manufacturers also use some additives to enhance its conductivity, unfortunately they don't disclose all the information on how they produce their PEDOT:PSS. The PEDOT to PSS ratio also has a direct influence on the conductivity of the polymer [69]. The low conductive PEDOT:PSS reflects a low population of conductive spots. This type is mainly used for antistatic coating.

2.5.1 Structure of PEDOT:PSS polymer

The PEDOT:PSS structure is shown in Figure 2.2. There is a positive charge on the PEDOT and a negative charge on PSS. The charge on the PEDOT is balanced by anions from PSS. The PEDOT part is assumed to be positively charged, with the active site appearing after every three or so molecules. The PSS counterpart is negatively charged.

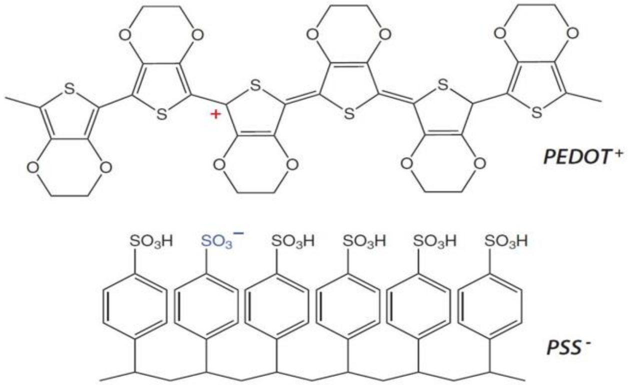
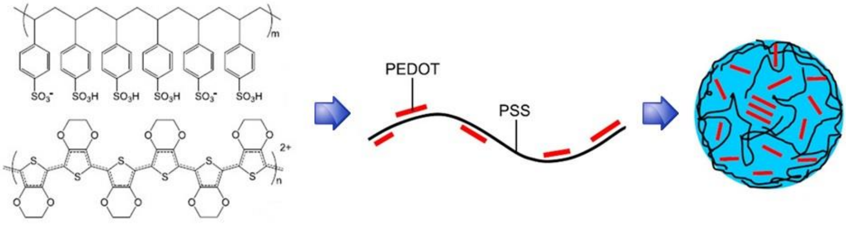


Figure 2.2 PEDOT:PSS chemical structure in electrically active state, there is a positive charge on the PEDOT and a negative charge on the PSS

2.5.2 Properties

PEDOT on its own is an insoluble polymer in water but it can be embedded into PSS using the Baytron-P process [70] to form a water soluble dispersion. The polyelectrolyte, i.e. polystyrene sulfonic acid (PSS) is a charge balancing dopant [71]. The dispersion is deep blue in colour. When PEDOT is doped with PSS it forms a complex micro dispersion in water which makes it good for spin coating of conductive films [69] and solution process ability in industrial processes.

The PEDOT:PSS dispersion is a colloidal suspension [71] in which there is excess modifiable PSS (see Figure 2.3). The PEDOT:PSS dispersions in water appeared as small particles and when left still for a long time, they settle at the bottom of the container. The particle sizes are in the range of 80-100 nm according to the suppliers. When PSS is used to dope PEDOT, only a small fraction of the PSS molecules actually bonds to the host PEDOT; the rest of the PSS molecules do not become ionized and are inactive. The PEDOT oligomers adheres to the PSS chain and coil up to form a tertiary structure see (Figure 2.3).



Sequence of monomers (Primary structure)

Poly-ion complex (Secondary structure)

Colloidal gel particles (Tertiary structure)

Figure 2.3 Primary and tertiary structure of PEDOT:PSS [Source[72]]

An increase of the PSS ratio decreases the conductivity, PEDOT:PSS ratios ranging from 1:2.5 to 1:20 imply conductivities in the range from 1 to 10^{-5} S/cm respectively [69].

PEDOT:PSS absorbs moisture from the environment (the higher amount of PSS the more it absorbs). After heat treatment, then exposed to air, they rapidly uptake atmospheric moisture [73].

2.5.3 Conductivity enhancement

Due to the importance of PEDOT:PSS and many applications, scientists are working hard to modify it and make it even better. The dilemma is that every time there is a successful improvement in enhancing its conductivity, the main science behind it is debatable. PEDOT:PSS conductivity can be increased more than an order in magnitude by adding polyalcohols i.e. alcohols with more than two OH groups, e.g. ethylene glycol, or by adding high dielectric solvents e.g. methyl sulfoxide (DMSO), dimethylfomaldehyde (DMF) and tetrahydrofuran, the enhancement ratio is dependent on the dielectric constant of the additive [74].

Pristine PEDOT: PSS in water has a conductivity of about 0.8 S/cm. Depending on the solvent type used the conductivity can increase up to 80 S/cm, however the polymer chain conformation does not change by the solvent used. This is important because the main polymer chain plays an important role in charge transport properties. The conductivity of PEDOT:PSS also depends on the preparation method [75], electropolymerised (80 S/cm) and chemically polymerized (0.03 S/cm) [71]. Ion transport in chemically prepared layers are found to be faster than in electrochemically prepared films. Chemically prepared PEDOT:PSS is likely to contain an excess of PSS which surrounds the PEDOT:PSS particle and forms a micelle. The insulating PSS domains give low conductivity compared to the electropolymerised PEDOT:PSS. Several attempts have been reported to increase the conductivity of PEDOT:PSS films and to improve their hole injection properties. The main methods used are [76]:

- chemically modifying the polymer during synthesis
- adding of small amounts of surfactants to improve the wetting effect
- mixing the PEDOT:PSS dispersion with on organic solvent like DMSO.
- adding a dopant to modify the morphology e.g. the sorbitol or glycerol

Kim *et al.* [74] proposed that the mechanism behind improvement of conductivity by addition of high dielectric constant solvents, induces screening effect between the positively charged PEDOT chain and negatively charged PSS chain, thereby reducing the coulombic interaction between the counter ions and the charge carrier. On the other hand Jonsson *et al.* [77] argued that the reason for the conductivity enhancement is that PSS chains are washed away from the surface region of the PEDOT:PSS film during the film-forming process so that a thin layer with high PEDOT:PSS concentration is formed on the fabric (Section 2.8 device fabrication, coating of 7 layers with drying in between layers).

PEDOT:PSS displays electron and ionic conduction which are the basic properties for its use in supercapacitors [78].

Great effort has been made to understand and improve PEDOT:PSS conductivity, which has been demonstrated to be tailored in a wide range between 0.1 and 4380 S/cm using solvent treatment [79-83].

2.5.4 Effect of heat treatment, humidity and air on PEDOT:PSS

When the polymer is subjected to rapid thermal processing it exhibits an increase in conductivity. Processing of PEDOT:PSS film at 200 °C for 30 s will result in a 35% increase in carrier mobility. Other material characteristics of PEDOT:PSS from electrical analysis, are found to be unchanged with the thermal annealing processing [84]. It has also been reported that sustained heating at 150 °C under atmospheric conditions causes irreversible structural changes in the PEDOT main chain [48]. The presence of water (humidity) and oxygen in the ambient air during annealing reduces the conductivity of the films. The hygroscopic nature of this polymer is from the PSS counterpart.

Despite the effect of humidity on PEDOT:PSS, no special packaging was used to protect the content of our fabricated cells from humidity and oxygen in the air. However, heating process while forming the PEDOT:PSS layers was controlled between certain temperatures which will be discussed in later chapters.

2.5.5 Recent research applications of PEDOT:PSS

PEDOT:PSS has unique electrical, electrochemical and optical characteristics which makes it have versatile electronic applications. It can be used as ion – to – electron transducers [85] with their immobilized ion recognition sites that induce selectively. The ion recognition sites may either be bonded covalently to the polymer backbone or entrapped as a doping ion in the polymer matrix [43]. The conjugated conductive polymers also play an important role as organic semiconductors. PEDOT:PSS is commonly used as an antistatic coating on electronic component packaging and also has been utilized as an electrode for the polymer batteries.

Other than the applications in energy storage where most researchers use PEDOT:PSS as an electrode material, the PEDOT:PSS has been used to make conductive threads. Recently in research silk threads coated with PEDOT:PSS have been used to make electrical interconnects for data and power transfer for intelligent/smart textile system. Silk fibers were coated with PEDOT:PSS, and the resultant yarn displayed significantly high electrical conductivity (9 S/cm) with physical robustness (yarn strength and modulus). The physical properties of the coated yarns were tested, i.e. yield strength, glass transition temperature changes, ductility, young modulus were insignificantly affected. The PEDOT:PSS dip-coated threads could withstand scanning at low voltages. Decomposition of the electrical conductor began at 4.0 V and the thread burnt 6.0 volts [86].

Conductive PEDOT:PSS multifilament yarns have been produced by wet spinning process. The PEDOT:PSS pellets were dispersed in polyvinyl alcohol and coagulated in a spinning bath of cold methanol. The produced blend yarns of PEDOT:PSS/PVA could be used as flexible electrodes in detecting human heart beat, or for wearable electronics [87].

The fact that PEDOT:PSS has varied conductivity based on PEDOT to PSS ratio, this aspect has been utilized to produce PEDOT:PSS for different specific applications areas which are shown in the Table 2.1below From Baytron® [69, 88].

Table 2.1 Applications of PEDOT:PSS based on PEDOT to PSS ratio Source [69, 88]

PEDOT:PSS Ratio	Solid content	Conductivity S cm^{-1}	Application
1:2.5	1.3	1	Antistatics
1:6	1.5	10^{-3}	OLEDS
1:20	3	10^{-5}	Passive matrix display

2.6 Electrode materials

As already discussed earlier, ***energy densities*** of energy storage devices are determined by the selection of electrode material. The two electrodes are denoted as the anode and the cathode.

Anode: cell electrode that releases electrons and is oxidized.

Cathode: cell electrode that accepts the electrons and is reduced.

These terminologies are used in battery and to a little extend in capacitors. In capacitors they are mainly the negative and the positive electrodes.

In capacitors, the two electrodes; anode and cathode can either be made from two different materials (asymmetric capacitors) or of the same material (symmetrical capacitors).

In this research, we used three different types of yarn electrodes.

- copper coated polybenzoxazole (PBO) yarns
- silver coated PBO yarns and
- pure stainless steel filament yarns.

Since the yarns were of different sizes, construction and diameters, a standard measurement was performed to determine the resistance per metre of each yarn. See Table 2.2

Table 2.2 Summary of yarn electrodes specifications

Type of yarns electrode	Copper coated PBO yarn	Silver coated PBO yarn	Stainless steel yarn
Measured resistance ohm/metre	1.7	3.4	9.7
Measured Resistance after coating with PEDOT:PSS ohm/metre	1.6	4.08	11.2
Yarn count (tex) grams/1000m	290	290	1000
Number of filaments	166	166	1100
Approximate Yarn diameter in µm	370	370	450

NB: The respective resistivity (resistance*area/length) of the metallic parts are: Silver 1.59*10^-8 ohm metre, Copper 1.68*10^-8 ohm metre, Stainless steel 69.0*10^-8ohmetre.(Source [89])

In the initial phase of this research, the yarn electrodes were combined in the devices construction as:

a) Same type of yarn filament as yarn electrodes, like in the symmetric capacitors and
b) Different types of yarn filament as yarn electrodes.

In most cases, a combination of different type of yarn electrodes (b) in one assembly could not yield good results and was therefore dropped. Throughout this study we decided to explore charge storage device with better result. Therefore an elimination method was followed.

2.6.1 Copper coated PBO filament yarns

These yarns were obtained from AmberStrand® company [90]. They are referred to as metal clad fibers. They are made from a number of very thin copper coated PBO filaments(about 10 µm diameter), bunched together to form a filament yarn. They are mainly applied in technical areas that require size and weight reduction, with strong and repeated flexure or at high temperature up to 200^0C. They are flexible, light weight and strong conductive yarns. The base material polybenzoxazole (PBO) is a high performance polymer with excellent heat resistant characteristics. The copper coated

PBO filament yarns target use in commercial jets and aircraft applications, where conversion from heavy metal to metal clad fibre from AmberStrand® company could mean ability to add one more passenger to each flight [90].

We used this filament yarn as yarn electrode in one set of the developed energy storage devices. The measured linear resistance of the copper coated filament yarns used is approximately **1.7** Ohm/metre.

2.6.2 Silver coated PBO filament yarn

Silver coated PBO filament yarns were also obtained from AmberStrand® company [90]. They are similar to the copper coated PBO filaments except that in this type they use silver metal to coat the PBO filaments. The measured linear resistance of this filament yarn is **3.4** Ohm/metre. Figure 2.4 shows the image of these conductive yarns from AmberStrand® company [90].

Figure 2.4 Metal clad fibers from AmberStrand®

2.6.3 Pure stainless steel filament yarns

Stainless steel material finds many applications in the ever changing technological world. Corrosion resistance is the main requirement in most of these applications. Steel exist in different types of alloys. Stainless steel is recognized by its chromium (cr) content, minimum 10.5%. The material is stable in a wide range of conditions and media due to the formation of Cr-rich stable passive films [91, 92].

Composition of **AISI 316L** steel grade is mainly made from iron and chrome, nickel and molybdenum in different percentages, the rest of the elements are traces and is the steel used to produce the pure stainless steel yarn electrode used in this research.

The pure stainless steel conductive yarns were supplied by Bekintex company [93]. The special brand name of the particular yarn used is BEKAERT BEKINOX® VN. They are made of continuous multifilament of pure stainless steel material. They are very flexible and strong. To produce these filaments, stainless steel is bundle drawn into fine filaments. Figure 2.5 shows a bobbin of one size of the stainless steel filament yarns

BEKAERT BEKINOX® VN. The filament diameters as claimed from the manufacturers patent are between 0.5 and 100μm [94]. A number of filaments are twisted together to form the filament yarns with different yarn counts. The different sizes of yarns have different yarn resistance per metre. These yarns are used in various applications; signal transfer, interconnects, power transfer, thermal conductivity, antistatic clothing and gas burner.

Figure 2.5. A bobbin of pure stainless steel filament yarns from BEKAERT BEKINOX® VN

All the mentioned conductive yarns were used separately as yarn electrodes in cell fabrication since the combination of different yarns in one device did not yield good results. The stainless steel conductive yarn was of our main interest since it performed better in charge storage in the developed cells, compared to copper coated PBO yarn electrodes and silver coated PBO yarn electrodes. These result could only be related to the material properties of the yarn electrodes, yarn specifications and their interaction with the chosen electrolyte - PEDOT:PSS.

Bekintex [93] is the original manufacturer of stainless steel filament yarns. From their patent [94], they give the percentage composition of various elements of the stainless steel yarn as shown in Table 2.3.

Table 2.3 The elements contained in the stainless steel yarn AISI 316L and their percentage composition.

Element	C	Mn	Si	Ni	Cr	Mo	Cu	N	S	P	Fe
%	≤ 0.05	≤ 5	≤ 2	8-12	15-20	≤ 3	≤ 4	0.05	0.01	0.05	Bal

These chemical elements in chronological order are: ***C*** *- carbon,* ***Mn*** *- manganese,* ***Ni*** *- nickel,* ***Cr*** *- chrome,* ***Mo*** *- molybdenum,* ***Cu*** *- copper,* ***N****- nitrogen,* ***S*** *- sulphur,* ***P****- phosphorous,* ***Fe****- iron.*

2.7 Textile substrate

The base material used to make the cell was a woven textile substrate. It acted as the carrier of the cell components and also as a separator between the two yarn electrodes, to prevent electrical contact between them. This support from woven textile ensured that the developed device was flexible, and well integrated into the textile matrix. Four (4) different types of woven textile material (see Table 2.4) were randomly chosen from the materials present in the textile department. The materials were tested for their ability to hold electrolyte in a confined area without spreading too much. These materials were not given any special treatment to enhance their absorption property. Normally the grey textiles are subjected to wet treatment to improve on their wetting properties, but this was not necessary in our experiments.

Three pieces (5cm by 5cm) of each textile sample material were laminated together in layers using an interlining adhesive (hot melt adhesive). A laminate structure was necessary because otherwise a single layer of the plain woven textile was too porous. Therefore, the three laminate structures reduced the sipping of electrolyte through the fabric. Another thin layer of thermoplastic polyurethane (TPU) obtained from Epurex company [95] was added on the upper part of the layered fabric. In this top layer, a region of 10mm by 6mm was left out, (not covered with TPU) for the application of the electrolyte. The aim of using the TPU layer was to make the surface hydrophobic so that the applied electrolyte, in the left out region is contained on the applied area only and does not spread much. The TPU was a good choice of material to give the hydrophobic property on the upper surface due to its lightness, flexibility and invisibility when fused on the surface of fabric. It was also a cheaper option to make the surface hydrophobic compared to other technologies like plasma treatment.

The ability of the layered textile substrate to contain the electrolyte in a confined region was directly related to the fabric properties. These properties are: type of material, fabric construction, yarn density and fabric porosity. Table 2.4 gives the material properties of the selected fabrics.

Table 2.4 Woven fabrics specifications

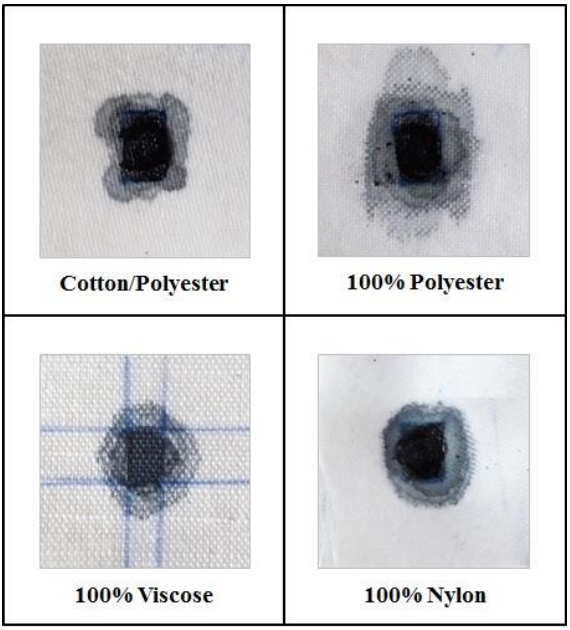
Fabric	Yarn Density of fabric		Type of weave	Thickness (mm)	Absorption capacity (%) [96]
	Warp (threads/ cm)	Weft (threads/ cm)			
Cotton/Polyester	42	29	Twill 3/1	0.414	161
100% Viscose	18	11	Plain 1/1	0.488	101
100% Polyamide	45	32	Twill 2/2	0.198	135
100% Polyester	46	25	Plain 1/1	0.380	127

Source [97]

From Table 2.4, the yarns used to produce the cotton/polyester blend fabric were less fine compared to the ones used for the polyester and nylon fabrics, and not too course like the ones used for the viscose fabric. However, the number of warp and weft yarns were more or less the same for cotton polyester blend fabric, polyamide and polyester. The thickness of the cotton/polyester fabric and the viscose fabric was in the same range, but the number of yarns per centimetre differed. The type of weave was also different.

Out of the four woven fabrics tested, the cotton/polyester blend fabric was selected, since it was the best in containing the electrolyte in the confined region. We cannot conclusively say that it is only due to the material type, but also due to the fabric construction parameters. Additionally, it was easy to sew the yarn electrode through this fabric compared to the polyester and the polyamide fabric.

The cotton/polyester fabric appeared to be the most suitable for our textile substrate. The yarns used for the fabric were medium in fineness, and the weave structure was medium-compact hence could allow easy insertion of yarn electrodes and controlled passage of the electrolyte through the fabric layers. The coarseness or fineness of the warp and weft yarns also had an influence on the porosity of the fabric. The appearance of the four woven fabric samples with applied electrolyte on them are shown in Figure 2.6.



Cotton/Polyester

100% Polyester

100% Viscose

100% Nylon

Figure 2.6 **Appearance of electrolyte spread on the fabric layers.**

All the fabrics had a minimized spread of electrolyte, but the cotton/polyester was less. All the fabrics could actually be used in the fabrication of the energy storage devices, if their fabric construction specifications were optimized, but that was not the focus of this research.

The number of warp yarns or weft yarns per centimetre if altered will influence the spaces in between the yarns, this subsequently determines how much of electrolyte coated will percolate through. The twists in the yarns would also determine how fast the yarns can wick the electrolyte. But this kind of variation in the fabric structure was beyond the scope of this research. Therefore, we picked on the most immediate suitable fabric for the textile substrate, the cotton polyester fabric.

2.8 Fabrication of the devices

Fabrics that were readily available in our lab were selected randomly; polyamide, cotton/polyester, and pure polyester fabrics with specifications given previously tested to choose the appropriate textile substrate. We settled for cotton/polyester because of the fabric structure and good fabric properties regarding to wettability and spread of the applied electrolyte, which allowed the PEDOT:PSS polymer to coat the fabric and be contained in the defined regions.

The **woven textile substrate** consisted of three pieces of cotton/polyester fabric (5 cm by 5 cm) which were cut from the main fabric. Additionally, two pieces of a hot melt adhesive interlining with same dimensions as the fabric, were used to laminate the three fabric layers together. Before laminating with the interlining, three yarn electrodes from the same type of yarn, approximately 6 cm in length were sewn into the surface fabric. Although two electrodes could be sufficient to fabricate the cell, three yarn electrodes were used just in case one contact of yarn electrode would fail. The yarn electrodes were sewn close to each other in a center region of the device as illustrated in Figure 2.7.

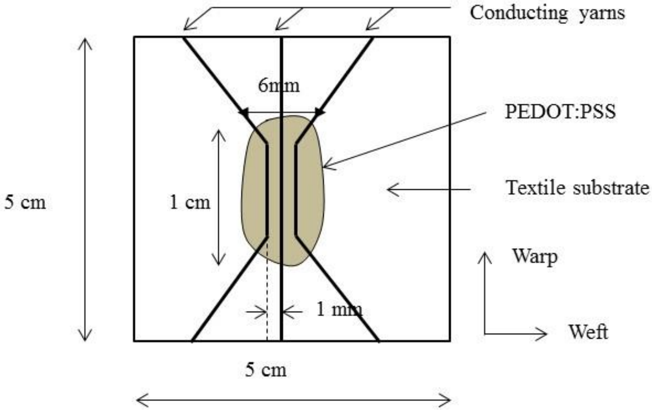
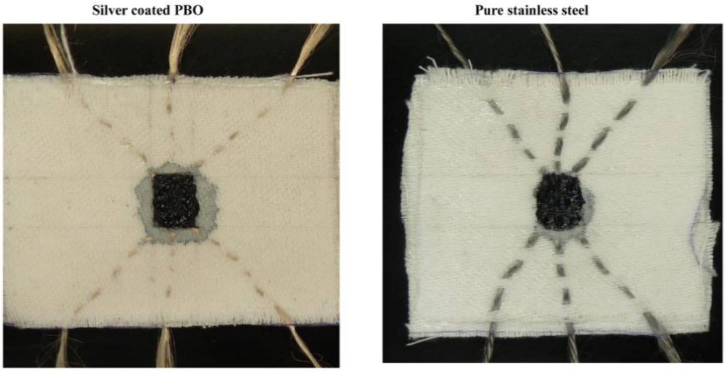


Figure 2.7 Design of the charge storage device.

For the **yarn electrodes** three types of conductive yarns were used; copper coated PBO filament yarn electrodes and silver coated PBO filament yarns from AmberStrand® company [90] and pure stainless steel filament yarn from Bekintex [93]. The material specifications of these conductive yarns are presented in Table 2.2 Summary of yarn electrodes specifications.

A defined active area of 10 mm by 6 mm was not covered with hydrophobic polymer at the center region of the textile laminate (see Figure 2.7 Design of the charge storage device.). The dimensions of the active area of the cell were borrowed from Bhattacharya *et. al* [37] and modified according to our methodology in later experiments. PEDOT:PSS electrolyte is to be coated on this region. The yarn electrodes separation distance within this active region was approximately 1 mm as shown in Figure 2.7 and the total yarn length within the coated region was approximately 10 mm. The upper surface of the fabric was made hydrophobic using a thermoplastic polyurethane (TPU) layer from Epurex film company [95], except for this center region of 10 mm by 6 mm.

For the **electrolyte,** PEDOT:PSS was drop coated systematically in layers in the left out region. A total of seven layers was coated to increase the PEDOT:PSS loading into the fabric, since the PEDOT:PSS dispersion was very light only 6% in water. Also the many coating layers increased the coating uniformity and reduced the bulk resistance. The PEDOT:PSS (about 0.5 ml) per layer was drop coated with a pipette uniformly on the fabric while it was in the oven. Each layer of PEDOT:PSS was left to dry in the oven for 15 minutes at a temperature of 90 -100^{0}C, before applying the next layer. Images of some of the produced charge storage devices from silver coated PBO filament yarn electrodes and pure stainless steel filament yarn electrodes are as presented in Figure 2.8.



Silver coated PBO

Pure stainless steel

Figure 2.8 Silver coated PBO filament yarn electrodes device and pure stainless steel filament yarn device.

In order to see a proper cross section and the interaction between the electrolyte and the textile substrate with the yarn electrodes, a Z - direction (depth) section of the pure stainless steel filament yarn electrode device was examined by stereoscope. A sketch of the same view is shown in Figure 2.9A, and the stereoscope cross sectional view of the device in Figure 2.9B. It can be seen that the PEDOT:PSS has covered around the electrode surface. The porous nature of the yarn electrodes enables increased surface area of yarn electrode.

A lot of caution had to be taken while sewing in the yarn electrodes, since in some devices the filaments of yarn electrode from the two opposite electrodes would touch due to the fibrous nature of the filaments and the close proximity of these electrodes in the design. In such cases there would be a short circuit and therefore no charge storage.

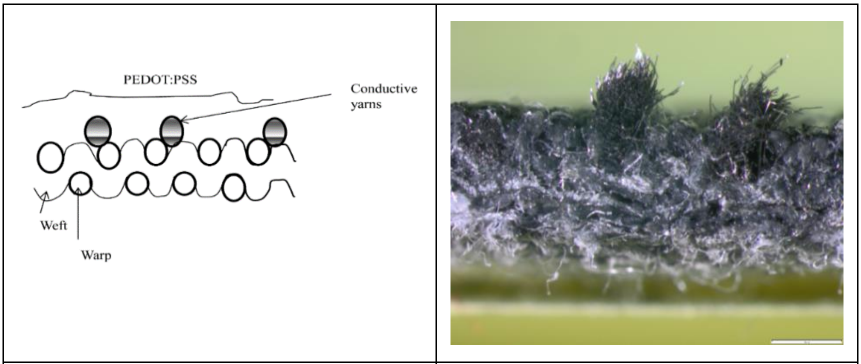


Figure 2.9A Figure 2.9B

Figure 2.9 Z direction (depth) section view of the cell from stainless steel yarn electrodes.

Neither the PEDOT:PSS layer nor the entire cell was covered by a protective layer, the cells were exposed to the ambient environment through out. But in future, it will be important to cover the cells to protect them from humidity and oxygen which has an effect on the PEDOT:PSS molecules. Protection is also needed for laundry as part of care if the textile garment with the cells in them would need to be washed, otherwise the polymer electrolyte easily disperse back to the solution, thereby reducing the current loading.

2.9 Conclusion

The materials used in the development of textile based energy storage devices has been explained according to their function given. The materials used have been discussed as: **Electrolyte:** PEDOT:PSS is used as the electrolyte. This polymer dispersion is complex, and with a wide range of properties depending on its composition. Different brands of PEDOT:PSS produced different results in the devices hence it was necessary to understand in detail the characteristics and application areas of PEDOT:PSS. **Yarn electrodes**: Three types of conductive yarns; copper coated PBO, silver coated PBO and pure stainless steel filament yarns were used as yarn electrodes in different sets of devices. **Textile substrate**: Cotton/polyester blend was selected out of the available fabric variety. A hot melt adhesive was used to laminate the three layered fabric while the upper surface of the textile substrate was made hydrophobic using thermoplastic polyurethane (TPU).

Fabrication: The energy storage devices were designed and fabricated using different types of yarn electrodes making them ready for research exploration and comparison.

3

Charge – discharge procedure of the charge storage devices

This chapter presents the initial experimental work that was performed on the developed devices. The devices were made from the different types of conductive yarns (copper coated PBO yarns, silver coated PBO yarns and stainless steel yarns) as yarn electrodes, with PEDOT:PSS as electrolyte. The developed charge storage devices were charged and their discharge characteristics observed. Three sets of devices were produced, based on a single type of conductive yarns and another three sets based on a combination of two types of conductive yarns. The sets of devices with combination of two different type of filament yarn electrodes did not perform well, hence will not be discussed in detail. Devices made with copper coated PBO yarn electrodes also did not store noticeable charge.

The devices were charged and their self-discharge was measured by voltage decay. The effect of varying the charging time, on accumulated charge in the devices will be presented graphically by voltage decay measurements over time for both silver coated yarn electrodes and pure stainless steel yarn electrodes. A comparison of the devices made with silver coated PBO filament yarn electrodes and the devices made with pure stainless steel filament yarn electrodes will be discussed.

Study of the effect brought by various load resistors on the voltage decay of the devices was also performed and is presented in this chapter.

In this research the devices made with pure stainless steel filaments yarn electrodes performed better than the devices with silver coated yarn electrodes. The possible charge storage mechanism of the developed energy storage devices will also be discussed.

This chapter is based on the publication:

Discharge characteristics of poly(3,4-ethylene dioxythiophene):poly(styrenesulphonate) (PEDOT: PSS) textile batteries; comparison of silver coated yarn electrodes devices and pure stainless steel filament yarn electrodes devices, Textile Research Journal 2014 (84) 347-354.

3.1 Introduction

Electronic devices integrated into textiles for example transistors, light emitting diodes, biosensors, and energy storage devices are generally made from electro-active polymers in combination with conductive materials under special fabrication methods [98-101]. These are incorporated or integrated into traditional textile substrates to produce high innovative products that are light weight and comfortable. These innovative products are referred to as smart textiles, textronics or electronic textiles [102, 103] in some literature.

The electro-active polymer, PEDOT:PSS which was chosen for this research has greater flexibility with respect to its chemistry and physics as discussed in previous chapter. This polymer was chosen since it has been shown that it can be used to manufacture polymer batteries and supercapacitors [59, 104, 105]. It has been used both as an electrode material (spin coated) [8, 59, 62, 67, 106] and as an electrolyte [37, 53]. It is a safer polymer to work with and more environmental friendly compared to carbon nanotubes that are used by other researchers [22, 45, 47, 107-109]. The polymer has good electrochemical stability, charge capacity and ionic conductivity [81, 110, 111].

Conductive stainless steel yarns are reported to be used in production of textile electrodes [112], electromagnetic shielding fabrics, heating garments [113] and smart garments for healthcare among others. They have the advantage of flexibility and comfort when made into fine filament yarns, and can be integrated into the fabrics by stitching, knitting or weaving [112-114]. They also have good electrical and thermal conductivity with high melting points. Silver coated yarns have also been used in smart textiles to get conductive tracks with low resistance compared to other conductive yarns, but they are more expensive than stainless steel yarns. Copper coated yarns have been produced at research level in our department [115] and also by various companies with aim of using them as conductive yarns in smart textile units production.

In this chapter copper coated PBO yarns, silver coated PBO yarns and pure stainless steel yarns are used as yarn electrodes in the fabrication of the charge storage devices.

Bhattacharya *et al.*[37] made a similar rechargeable textile battery using PEDOT:PSS as an active electronic coating and silver coated polyamide yarns as electrodes, on a textile substrate [37]. The textile substrates were three layered jacquard fabrics with a weft density of 40 yarns/cm and a warp density of 50 yarns/cm. The basic yarns in the fabric were 78 dtex twisted polyamide fibers. Interwoven with these yarns were silver coated 235 dtex polyamide fibers with a conductivity of approximately 15–20 S/m which were used as yarn electrodes for the fabricated charge storage device. This device was simple in design, but not in the production process, the woven textile substrate was produced by jacquard weaving where the yarn electrodes were inserted in the weaving process.

We reproduce a similar device with PEDOT:PSS electrolyte and silver coated yarn electrodes using a simplified technology as a starting point, later we made similar devices using different types of yarn electrodes and compared the results. This was our first step towards achieving a light, textile based energy storage device.

This research shows that the combination of PEDOT:PSS and stainless steel yarn electrodes in the charge storage device gives better results compared to the silver coated PBO filament yarns. Copper coated yarn electrodes did not store any charge at all.

3.2 The general charge - discharge procedure

3.2.1 General

The developed devices were charged normally as it is done with batteries before use. Therefore a ***power source*** was required for this operation. When the developed cell is completely charged, the energy stored in it was measured, ***a voltmeter*** was used to measure the voltage in the devices before and after charging. The experimental set up is as indicated in Figure 3.1. The device is connected to the power source and to the voltmeter in parallel connection. A digital camera was used to record the voltmeter reading over time.

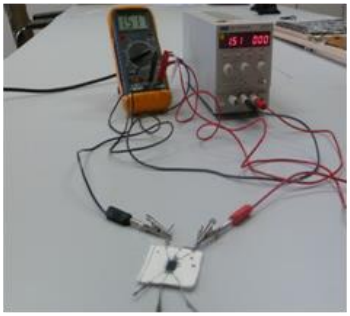


Figure 3.1 Charging set up

First of all, the voltage across the yarn electrodes of the developed devices was measured before charging and they were not having any stored charge. Therefore the assembling process did not create any charge in the device, the cells have to be charged. The circuit connection of the cell to the power supply and to the voltmeter is as shown in Figure 3.2. The connected device was then charged using the power supply PL601 always at a constant voltage of 1.5 V and for roughly 2 hours by closing the switch *S* (see Figure 3.2).

After the charging process, a voltage metre with a high input impedance of 10 MOhm was used to record the voltage *V* across the device. The recording started immediately after opening of the switch *S* at the initial time *t =0* .

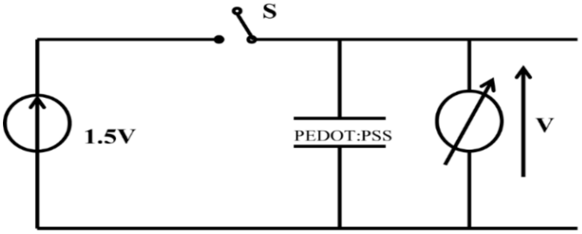


Figure 3.2 Schematic layout of charge - discharge.

In later chapters the use of a digital camera for recording the data of the voltage decay was replaced by use of equipment from National Instruments (NI) see Figure 3.3.The digital camera came in handy in the initial experiments as much as it was not very efficient since it entailed spending many hours recording the data manually from the camera video. Therefore a program was developed to run with the NI equipment in collaboration with bachelor students who programmed this equipment. The program enabled the equipment to charge the developed cells at specified voltages and time(s) and also captured the voltage decay data automatically. This was quite a relief because the charge - discharge times were too long (2 hours of charging and up to 5 hours of discharging). The apparatus NI PXI from National Instruments was used to carry out the operations automatically. The NI PXI 1033 is a chassis equipped with several voltage generators, a digital voltage metre and a computer interface. A relay was used to act as a switch of the circuit. The relay was controlled by one of the voltage generators.

Figure 3.3 National Instrument NI PXI

One may argue that charge storage is possible with blank samples without electrolyte in them. To investigate the dependence of charge storage in the device on the electrolyte PEDOT:PSS, a few blank devices were assembled with the yarn electrodes but without the electrolyte. These devices were charged for 2 hours and left to discharge. Essentially these devices could not charge, therefore they did not store any charge in them.

3.2.2 Results of charge - discharge experiments

The graphs show the voltage value in the cells at a given time in the discharge process. An immediate observation from the graphs is the sharp decrease of the voltage *V* in the beginning of the discharging curve, as soon as the switch *S* is opened (a few seconds). But after some time, in the range of 1 000 seconds, the voltage *V* is decreasing very slowly. This is true only for silver coated yarn electrodes and pure stainless steel filament yarn electrodes.

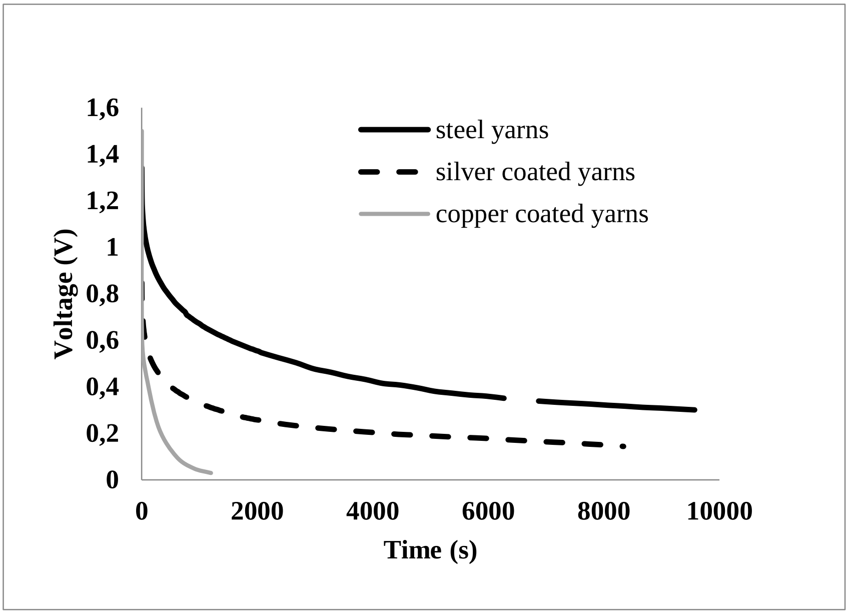


Figure 3.4 Voltage decay curves: comparison of the three different devices from different types of yarn electrodes , charging at 1.5 V for 2 hours then discharging.

The copper coated yarn electrode devices could not store any charge as can be seen in Figure 3.4. The charging process of the devices with copper coated PBO yarn electrodes went on well for a duration of 2 hours at 1.5 V. The voltage and the power supply were at the same voltage during charging process similar to the devices from the other types of yarn electrode especially when there is no short circuit in the device. This condition is not true in case of a device with short circuit between the electrodes, if current flow between the electrodes, the power supply and the voltmeter would have different readings.

The discharge of all the cells is very fast in the beginning just after switching off the power supply. After some time the discharge is proceeding very slowly. For the stainless steel yarn electrodes the voltage drops from 1.5 V to 0.4 V after one hour see Figure 3.4 which is a rather low efficiency if one would use the cell for electric energy storage, However the retained charge in stainless steel yarn electrode device is higher than the silver coated yarn electrode device.

3.3 Effect of variation of charging time

In another set of experiments, charging was performed at 1.5 V but the charging time t_{ch} was varied according to the experiment in question. The variation of time was between 5 minutes and 240 minutes at foreseen random intervals. The cell was left to discharge over long time after the charging process.

3.3.1 Device with silver coated PBO yarn electrode charging time variation

Devices with silver coated PBO yarn electrodes were charged at a constant voltage of 1.5 V for different durations (between 5 minutes and 240 minutes) with the circuit connection presented in Figure 3.2. A voltage metre with a high input impedance of 10 MOhm was used to record the voltage V across the device during discharge after the power supply was switched off by opening the switch S, at initial time $t = 0$.

In our initial experiments we used a reasonable ample time of 2 hours for charging, however in the process of trying to discover the charge storage mechanism, we decided to vary the charging time within the range given, to find out the effect of charging time on the charge storage in the devices, bearing in mind that capacitors charge in a shorter time than the batteries, since there is no chemical reaction in the capacitors as discussed in chapter one.

The voltage decay results obtained with the silver coated yarn electrode devices are shown in Figure 3.5, which shows the behaviour of the voltage decay of the devices in the first 5 000 seconds of discharge, starting just after the switch is off, and Figure 3.6 shows the voltage decay over a longer period of time up to 15 000 seconds. The results shows how a typical silver coated yarn electrode device behaves in the discharge process, and the effect of varying the charging time on the charge storage.

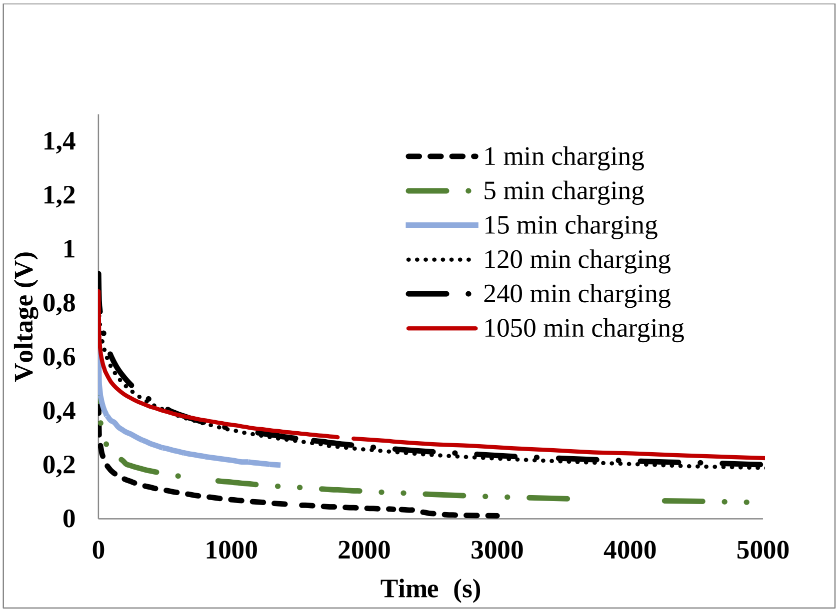


Figure 3.5 Voltage decay behaviour for the first 5 000 seconds for devices made of silver coated PBO filament yarn electrodes at various time of charging.

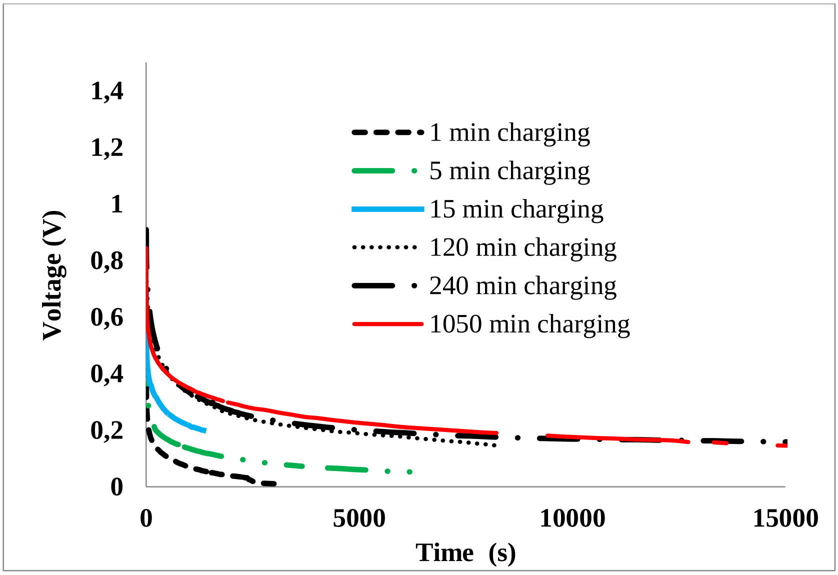


Figure 3.6 Voltage decay for up to 15 000 seconds for device made of silver coated PBO filament yarn electrodes, at various time of charging

The longer the charging time the slower the voltage decay and the higher the charge stored in the devices. However, after 2 hours of charging, any further increase in charging time led to insignificant increase in the accumulated charge, and again this charging was done at fixed voltage of 1.5V.

The results show possibility of a slow mechanism in the charge storage principle, which could be associated with movement of large ions. If the device was a pure capacitor, it is expected to fill up in a short time, therefore no much variation in charge storage based on charging time, but again we did not optimise on the charging voltage, we used a constant voltage of 1.5 V in the charging process.

All the curves show a similar voltage decay behaviour. The charge - discharge process can be repeated several times at 1.5 V and for 2 hours charging (up to 10 times). The discharge time is relatively long as can be seen in the graphs. These number of cycles (10 cycles) is comparable to the number of cycles reported by Liu *et al.* [25] in their solid electrolyte-based lithium batteries, and also slightly comparable to the cycling voltammetry measurements by Bhattacharya *et al.* [37].

3.3.2 Devices with stainless steel yarn electrode charging time variation

The voltage decay characteristics of devices made with pure stainless steel filament yarns are shown in Figure 3.7 & Figure 3.8. These devices were also charged at 1.5 V for different times of 5 minutes, 120 minutes and 240 minutes. The behaviour of the output voltage is similar to the silver coated PBO filament yarn electrodes device, but the values of charge stored are higher, again for a normal capacitor, we expect that after charging, the device is fully charged to the level of the charging voltage say 1.5 V in our case, and an insignificant discharge should occur if not connected to any load (see chapter one, Table 1.1 Parametric comparison of various forms of energy storage The maximum charging time of 2 hours at 1.5 V is also true for the stainless steel yarn electrode devices, after which, the increase in accumulated charge is insignificant. The curves for the stainless steel filament yarn electrodes remain at a constant voltage of 0.4 V for quite a long time, compared to the silver coated PBO filament yarn electrodes whose decay tends to remain constant at 0.2 V. These devices can be used for voltage stabilization for one hour if the load resistor is not too small.

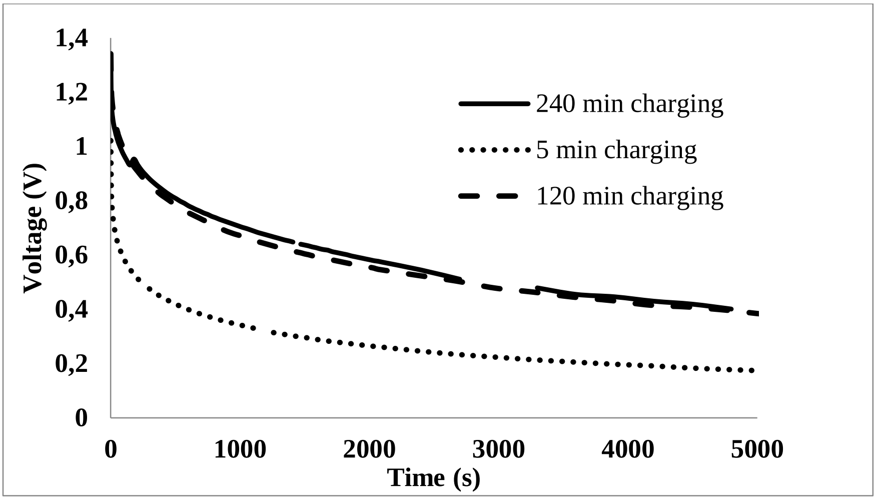


Figure 3.7 Voltage decay for the first 5 000 seconds for pure stainless steel filament yarns devices, various time of charging.

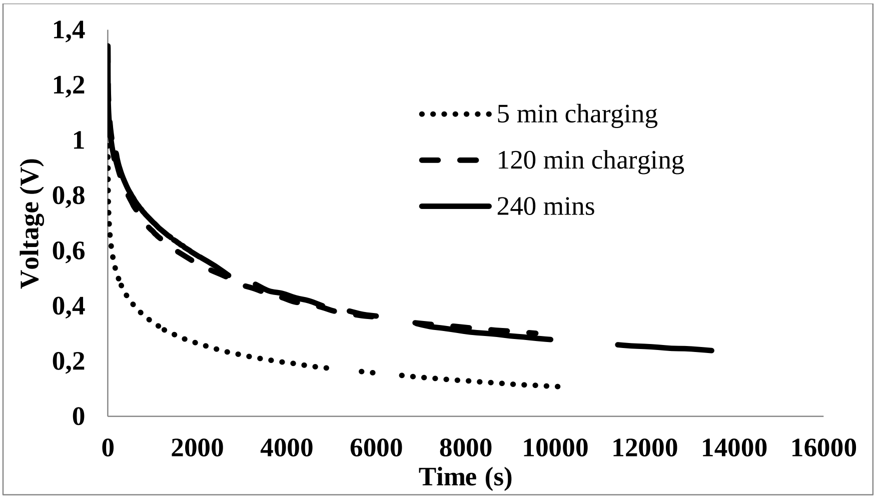


Figure 3.8 Voltage decay for pure stainless steel filament yarns device for 15 000 seconds discharge at various time of charging.

3.3.3 Comparison of devices with silver coated PBO yarn electrodes versus devices with pure stainless steel filament yarn electrodes.

When comparing the voltage decay of the two mentioned sets of devices as shown in Figure 3.9 , it is clear that the stainless steel yarn devices give better results than the silver coated PBO yarn electrode devices. The stainless steel yarn electrode devices can store charge for a longer period and with higher voltage values than the device with the silver coated PBO yarn electrodes. This shows that the mechanism that enables charge storage in the devices depends on the compatibility of these assembled materials in the developed cell, and also depends on if the charge storage is via electrochemical reactions or not. Remember in our chapter one, it was stated that the rate at which electricity can go in and out of the cell, is dependent on the chemistry behind it. Generally all the reactions in different types of metals from metal ion to metal solid is potential specific, we may argue that certain elements are reduced or oxidized within these cells, but that depends on whether we are having a reaction in the first place.

For both the devices, the longer the charging time, the more the stored charge until a certain limit. This can be clearly seen in the comparison in Figure 3.9 and Figure 3.10, the first Figure 3.9 shows comparison of voltage decay after charging for five minutes and the second Figure 3.10 shows the comparison of the voltage decay of the two devices after charging for 120 minutes.

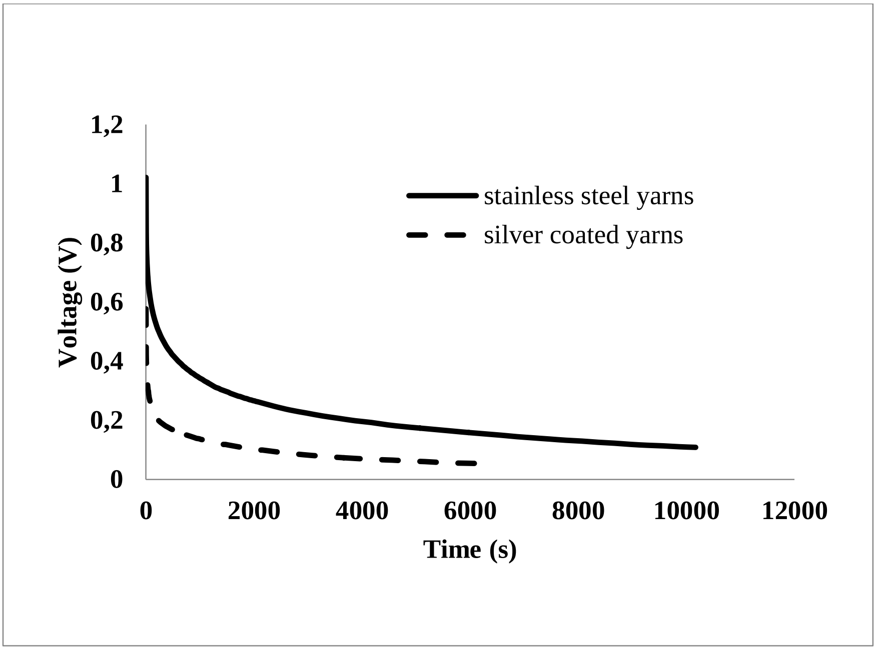


Figure 3.9 Comparison of voltage decay for silver coated PBO filament yarn electrode device and pure stainless steel filament yarn device for 5 minute charging time.

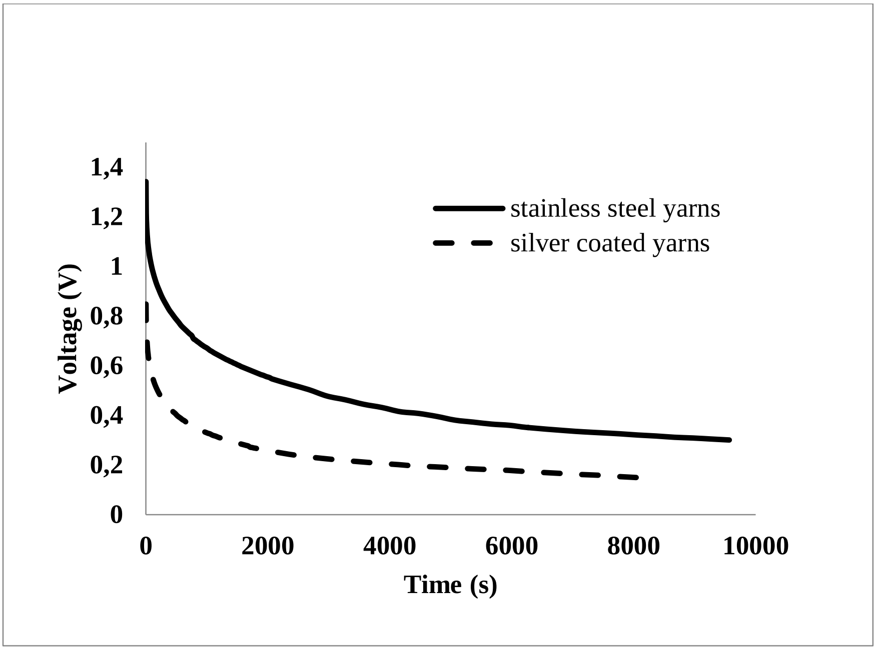


Figure 3.10 Comparison of voltage decay for silver coated PBO filament yarn device and pure stainless steel filament yarn device for 120 minutes charging.

The voltage discharge of all the cells is very fast in the beginning just after switching off the power supply. After some time the discharge proceeds very slowly. For the stainless steel yarn electrodes the voltage drops from 1.5 V to 0.4 V after one hour (see Figure 3.10) which is a rather low efficiency if one would use the cell for electric energy storage. The fast transient measurement in the very beginning is typical for a diffusion process and probably this fact is responsible for the low efficiency of the cells. This mechanism will be discussed in detail in the expected charge storage mechanism section. Anyway it must be pointed out here that the basic mechanisms occurring in the PEDOT:PSS devices are still not completely known. The cells with stainless steel filament yarn electrodes were found to be twice as good compared to the cells with the silver coated PBO filament yarn electrodes.

The difference in performance between stainless steel filament yarn electrodes and silver coated yarn electrodes could be explained by the electrolytic phenomenon observed by Bhattacharya [37], in their electron microscope measurement, they clearly observed migration of silver particles, with the silver coated yarn electrodes. PEDOT:PSS acted as an electrolyte that silver could migrate through in the presence of an electric field. There was also a possibility of chemical interaction at the silver/PEDOT:PSS interface. However with the stainless steel filament yarn electrode, it is not clear if the electrolytic phenomenon exists in the first place, but this opens up the complexity in the mechanism of charge storage in this fabricated devices. Never the less we realized that the stainless steel filament yarn had better performance in the fabricated cells. We will explain later the expected charge storage mechanism with regard to pure stainless steel filament yarn electrodes.

A similar conclusion of good performance of pure stainless steel filament yarn electrodes has also been reported in sensors for medical application [112]. It will be shown in section 4.3 that the pure stainless steel filament yarn electrodes are more robust, and could withstand many cycling of charge discharge compared to the silver coated yarn electrodes. The silver coated PBO filament yarn electrodes devices yielded before the stainless steel filament yarn electrode devices.

3.4 Experimental results with a load resistor

In another set of experiments, we aimed at establishing the size of load the developed device could support and for how long it could support it. Different sizes of load resistors were used in these experiments. The load resistor *R*, was always connected in parallel to the cell as shown in Figure 3.11. The cell connected was charged for 2hrs and then left to discharge. In the initial stages of this research, the voltage decay measurements were recorded by a camera. The readings were recorded from the voltmeter (multimetre digitool digi 16). The charge - discharge procedure was repeated up to three times on each device that was tested for these experiments. Normally in this we confirmed that the developed devices were rechargeable, and the voltage decay result were more or less the same with no significant change in the profile. However, at this point it was not established how many times the device could be recharged.

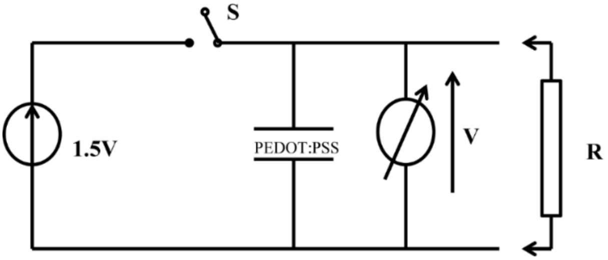


Figure 3.11 Circuit connection with load resistor

The load resistor experiments were carried out as a way of quantifying the amount of useful residual charge in our cells. We could not easily calculate the power stored within the cell after charging, due to the voltage decay behaviour of the developed cells. Also for the fact that we were still doubting if the developed device was a battery or a capacitor, as it can be seen in our first chapter, the two have different ratings, hence requires different approaches in the efforts to quantify the energy in them.

From the experiments done so far it is obvious that the PEDOT:PSS is self-discharging and the input impedance of the voltage metre is very high. To quantify this self-discharge, a resistor *R* (Figure 3.11) one at a time of 978 kOhm, 268 kOhm and 100 kOhm was connected in parallel with the PEDOT:PSS cell. After charging for 120 minutes at a constant voltage of 1.5 V, the decaying voltage *V* was recorded with the resistor connected. Devices with silver coated PBO filament yarn electrodes could not support the load resistors. These results are not shown, because these specific devices could barely support a load resistor. This could be due to the fact that silver coated yarn electrode being a better conductor (lower resistance 3.4 Ω/m) than the stainless steel electrode 9.7 Ω/m), it could release the little stored charges faster (say in milliseconds). This could not be easily observed. Additionally the silver coated yarn electrodes had less amounts of stored charge in them.

The obtained voltage decay curves from pure stainless steel filament yarn electrodes device are shown in Figure 3.12 & Figure 3.13. It can be observed that the decay is faster at the initial phase of the curve as it was without the resistor, but with lower values. It can also be observed that the lower the load resistor *R* the faster the voltage decay (analogous with ohms law). This means that the device can only power high load resistors which require very little current and therefore can be used for voltage stabilization if the resistor is not too small.

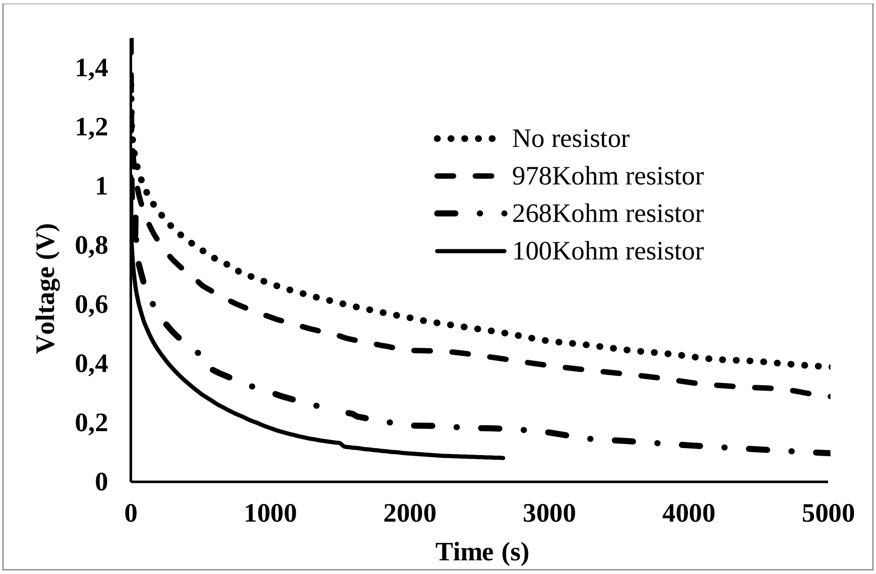


Figure 3.12 Result with load resistors for pure stainless steel filaments yarn electrodes device, voltage decay behaviour for the first 5 000 seconds.

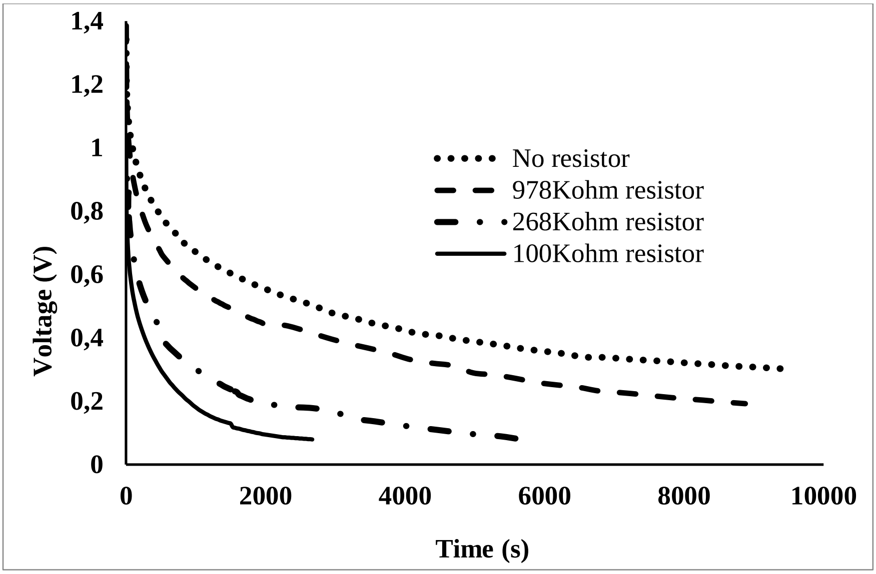


Figure 3.13 Result with load resistors for pure stainless steel filament yarn electrodes device, voltage decay behaviour for up to 10 000 seconds.

In all experiments done so far, the voltage metre with its input resistance of 10 MOhm was connected to the devices. One may wonder if we were dealing with a self-discharge of PEDOT:PSS cell or a discharge through the 10 MOhm input resistance of the voltage metre. Therefore, a different discharge experiment was done according to the connection circuit. The voltage metre was disconnected regularly for periods of 5 minutes. The metre was only connected for a short time, just enough to measure the voltage. The voltage decay graphs obtained with this experiment turned out to be almost coinciding with the curves shown previously. The conclusion is that we were really measuring the self-discharge of the PEDOT:PSS cells. The voltage metre has a negligible influence, it can be stated that the PEDOT:PSS cell has itself an internal resistance much lower than 10 MOhm.

From the discharge curves obtained with different values of the load resistor, the internal resistance of the PEDOT:PSS cell could be estimated to be around 300 kOhm. From most of the graphs of the voltage decay, one can observe time constants in the order of 1 hour or 3600 s. If the cell would be considered as a capacitor *C* connected in parallel with a resistance *R* of 10 MOhm, one has: $\tau = RC = 3\ 600$ s

Using the capacitance equation $\boldsymbol{V = V_0\, e^{-t/\tau}}$

Equation 6

where V is the voltage at any point within the curve for a perfect capacitor, V_0 the initial charging voltage, t time and RC the time constant, from which we get an estimated value of the capacitance (C) as 360μF.

This is a quite high value taking into account the limited area of the electrodes in contact with the dielectric/electrolyte. A possible conclusion is that only electrolytic phenomena could be responsible for such a high value, i.e. mobile ions (in strong ionic electrolyte) move under the influence of the applied electric field. However, this does not exclude the possibility of the combined electrochemical and capacitive effect as in the case of pseudo capacitors as discussed in chapter one. Also if there is an electrochemical effect it would be a unique one and basically within the electrolyte material, since the yarn electrodes were from the same material and the positive and negative electrodes could be interchanged in the experiments. This can never happen in a conventional battery or supercapacitor, an explosion may occur.

Cyclic voltammetry is one of the methods that could be used in categorizing the electrolytic phenomena, but it was not used to characterize the developed devices due to the enormous time constant involved.

3.5 Proposed charge storage mechanisms in the developed cells

The mechanism of charge storage in these developed devices is complicated, for now we can describe it in three phases, as a result of:

- Electrochemical reaction between the electrodes and the electrolyte as per Bhattacharya`s *et al.* [37] explanation,
- No reactions, but electrolyte ions separation, and formation of EDLC or
- Electrochemical reaction within other elements in the electrolyte and the electrode material.

First Bhattacharya *et al.* [37], described the process responsible for the charge storage in their device with silver coated yarn electrodes, is the presence of metallic silver in the PEDOT:PSS matrix. Also they reported that silver ions are migrating from one electrode (anode) and deposited on the other electrode (cathode). They claim to observe larger concentrations of silver on the cathode and not on the anode in the first recharging period implying that the PEDOT acted as an electrolyte that silver can migrate through in the presence of an electric field. The metallic silver movement present in the PEDOT layer is consistent with the expected chemical interaction at the Ag/PEDOT interface shown in other research works. It has been shown that silver and silver compounds in contact with PEDOT will diffuse as silver ions into PEDOT via charge and mass transfer processes [39-41]. “When a high electric field is applied to the PEDOT, the silver ions will diffuse through the PEDOT, from the anode to the cathode and recombine with electrons to become mostly silver metal” [37].

These phenomenon could be justifiable with silver coated yarn electrodes, but with pure stainless steel yarn it was complicated to identify which element were reacting since it is an alloy, and contains many elements. However, in our proposal we identified that this particular steel type used in our yarn electrode has a high percentage of chrome, and there could be a very thin chrome oxide layer on the yarn surface. Therefore, strong indication from our results is that the mechanism involved in the charge storage is mainly through separation of ions within the electrolyte and then the ability to form electric double layer on the electrode surfaces based on EDLC charge storage principle discussed in chapter one, section 1.4.1 Classification of capacitors. Therefore, we discussed the charge storage process differently (contrary to Bhattacharya's *et al.* [37] discussion), as mobile ions of PEDOT:PSS moving under the influence of the applied electric field. This does not rule out, the fact that there could be other elements within the PEDOT:PSS that enables this charge storage mechanism, since we also find out in upcoming chapter that not all types of PEDOT:PSS are able to produce this charge storage devices. It has already been discussed in detail the variability of this polymer and for the fact that different methods are used by the manufacturers to improve their conductivity. This product mix information is partially disclosed to the users of the material, hence the third mechanism that could be involved in the charge storage, which has not been proven though in this research, could be from the reaction from the elements within the electrolyte.

We are in the favour of the second mechanism, where we expect no electrochemical reactions. We concluded that during charging, the PEDOT which is positively charged ion and PSS (negatively charged) ions re-orient themselves or diffuse to the opposite electrodes. The chemical structure of electronically active PEDOT:PSS polymer is presented in Figure 3.14.

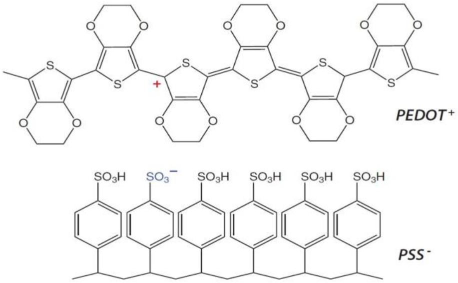


Figure 3.14 PEDOT:PSS chemical structure

Due to high molecular weight of the polymers involved, the movement of PSS from PEDOT and to the positive electrode takes a long time. This explains the longer time required to charge the device, (see the results with variation in voltage decay based on the charging time) the longer the charging time, the more the charge stored.

During the charging process, the ions are oriented according to their polarity and it takes sometime before they are fully oriented. In the discharge phase, the ions take even a longer time to go back to their original position, the discharge voltage will reach to zero anyway after a very long time. The charging time of these devices also has an influence on the voltage decay, the more time for charging the more charge is stored in the cell until a certain limit of charging time.

The charge storage also depended on the surface area of the yarn electrode.

The obtained results with the stainless steel yarn electrodes can be attributed to the various aspects of the developed devices. A possible explanation is that stainless steel is a combination of different elements (nickel, chromium, manganese and iron) hence not chemically inert. Therefore like any other non-inert metal, it will form an insulating (passivation) layer interface between the metal and the polymer [60, 116]. The pure stainless steel material is covered by a very thin layer (of a few nanometres) of chrome oxide (Cr_2O_3), that inhibits further oxidation of the steel. Cr_2O_3 is an electric insulating material, if made as a very thin layer (a few nanometres) it creates an electrode/insulator(oxide)/electrolyte interface in the device see (Figure 3.15). Electric conduction becomes possible through special mechanisms like the Schottky effect (Schottky effect is the increase in thermionic emission from a solid surface due to the presence of an external electric field) which brings change in electrostatics between a metal/semiconductor interface or through field emission [117].

It was mentioned recently in literature that the diffusion of silver ions into PEDOT:PSS would be responsible for the charge storage [37, 40, 43]. However, results obtained with stainless steel yarn electrodes prove that this cannot be the only conduction mechanism in the PEDOT:PSS device. Charge storage is possible with yarns from stainless steel filaments too, and even gives better results.

A possible mechanism of charge storage in the devices could be that PEDOT:PSS behaves like a dipole. Initially before electric charging, the molecules are randomly arranged. On application of an electric field, polarization takes place, the cations PEDOT+ are attracted to the negative electrode while the anions PSS- are attracted to the positive electrode. Given that the stainless steel filament yarns are covered with a thin film of chrome oxide, as shown in Figure 3.15, when the device is charged an electric double layer is observed in both the electrodes as shown.

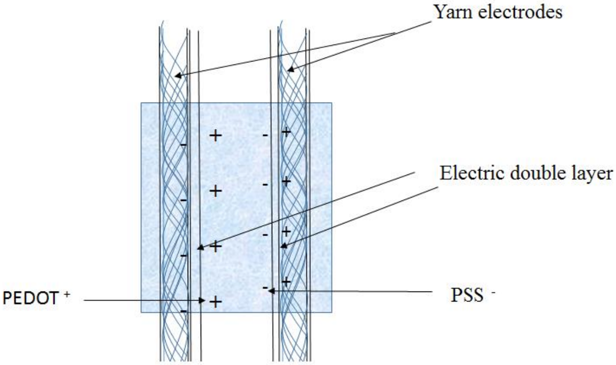


Figure 3.15 Electric double layer mechanism in the PEDOT:PSS device

The positive PEDOT and negative PSS ions being quite large molecules as shown in Figure 3.14, explains the low mobility and the long time needed to disorganize them. The charging process brings in a dielectric polarization of PEDOT:PSS, and on release, relaxation takes place as the molecules try to get back to their original random orientation.

Some differences in the performance of the silver coated yarn electrodes compared to the stainless steel filament yarns could be due to the difference in the ohmic contact between the PEDOT:PSS polymer and the different types of yarn electrodes [118]. Anyhow, it must be emphasized here that the physics of PEDOT:PSS is still under debate as claimed by other authors [81, 111]. Therefore our attempt to explain the mechanisms of charge storage may not be conclusive.

The overlapping C=C double bonds in the material provides π-orbital along the molecule which enables easy charge/electron transport. The regularity of the material structure has been associated with its outstanding chemical stability [119]. In oxidised state, the polymer molecular backbone is loaded with mobile carriers (holes) which makes it electrically conductive.

Some authors report that, due to the difference in rigidity between PEDOT and globular PSS, it is expected that several PSS coils will be associated with one given PEDOT molecule [88].

The conductivity of PEDOT:PSS depends highly on the polymerization process (chemical polymerization or electrical polymerization) [119] [80], purity of the product, the ratio between PEDOT and PSS, and the application process among others.

A capacitive process occurs in the electro-conductive polymer coating (PEDOT:PSS) on the textiles associated with movement of charge carriers to the interface between the polymer and the yarn electrodes. It is generally understood that the material is called

PEDOT whereas the PSS is the doping component. The PEDOT material can be doped with other chemicals too for other applications [78, 116].

The behaviour of the charge storage varies with the type of material interface, i.e. steel/PEDOT:PSS or silver/PEDOT:PSS. SEM-EDX imaging and FTIR spectroscopy in some literature has confirmed ion transport and redox reversibility in PEDOT:PSS [81, 120]. However the type of material of yarn electrode also contributes to the rate of the ion transport. Over-oxidation of this polymer causes irreversible deactivation of the polymeric coat, and hence the mechanical breakdown of the devices.

3.6 Conclusion

Textile-based energy storage devices were fabricated with PEDOT:PSS as the electrolyte, conductive yarns as yarn electrodes and textile substrate. Copper coated PBO filament yarns, silver coated PBO filament yarns and pure stainless steel filament yarns were used as yarn electrodes to produce different sets of devices. These charge storage devices were well integrated into a textile structure making them light weight and flexible. The devices could be easily fabricated.

From the results the developed cells experienced a self-discharge, the copper coated yarn electrodes could barely store any charge. Stainless steel yarn electrode devices performed better than the silver coated yarn electrodes device. They maintained a charge of at least 0.4 V while silver coated devices had about 0.2 V. The stainless steel yarn electrode devices could also support load resistors.

The developed devices had no predefined polarity. Both electrodes could be used for positive or negative electrodes and reversed if need be. As a consequence one may not denote the electrodes as cathode or anode, because they are both made from the same material.

One may wonder why we are using the term device and/or cell to refer to the developed energy storage devices instead of either a “battery” or a “capacitor”. This was a difficult decision to reach at, bearing in mind that we started from a defined battery principles by Bhattacharya´s *et al*. But since we are using two electrodes made from the same material, strictly speaking we were then dealing with a capacitor. On the other hand we could not exclude that some electrochemical reactions could be taking place in the device, because the physical mechanism of charge storage in PEDOT:PSS is still not well understood.

4

Stability and reliability testing of PEDOT:PSS capacitors integrated into textile fabric

After conducting experiments with the three different types of filament yarn electrodes, stainless steel filament yarn electrodes were found to be the best yarn for further experiments. They demonstrated outstanding charge storage in the developed devices, however they also experienced a self-discharge. It was useful to determine how consistent and reliable the devices were in terms of charge storage, and how many times we could charge – discharge them.

Additionally, the effect of recurrent charge - discharge cycles on the devices were investigated, and the reliability in the performance of the devices studied. If the devices were to be compared to the current conventional capacitors, they are expected to withstand thousands of these charge - discharge cycles. The developed devices with stainless steel yarn electrodes were charged - discharged repeatedly (on one device) for up to 14 cycles successfully. Initially the voltage output turns out to be higher with increasing number of cycles, however, after the fifth cycle the degradation of the cell starts occurring and a decreasing behaviour in the voltage output is observed. One can roughly say that these capacitors could be used for up to 10 - 15 cycles.

If the developed charge storage devices were to be used in the normal wear, they are expected to withstand washing and drying too which happens at temperatures higher than room temperature. Washing is an essential procedure to the garments to maintain them clean. For this purpose, a procedure towards studying the wash ability of the cells, and another one on exposure to higher temperatures between 30^0C and 40^0C was performed. As a first step to test washability, the effect of dipping the uncovered cell in water was studied and presented in this chapter. The effect of exposing the devices to higher temperatures are reported here too.

This chapter is based on the article:

Odhiambo, S. A.; De Mey, G.; Hertleer C.; Schwarz, A.; and Van Langenhove L., “Reliability testing of PEDOT:PSS capacitors integrated into textile fabrics. EKSPLOATACJA I NIEZAWODNOSC-MAINTENANCE AND RELIABILITY. 2014;16(3):447–51

4.1 Introduction

In recent years a lot of effort is put to integrate electronic components into textiles, a new discipline called textronics. The applications of smart textiles system can be found in many fields: protective clothing, medical applications and sports clothing as already mentioned in chapter one. An in depth overview can be found in literature [103, 115, 121, 122].

Robustness (ability to withstand, mechanical, chemical or electrical stresses without failure) and reliability (trusted performance) of electronic components is desired hence there is a continuous improvement in materials used to produce these components [123-126]. Additionally, understanding the effect of re-current stressing of a product, be it mechanical stress or electrical stress is an important aspect in determining the expected behaviour of a product or the life span.

Durability to laundry or washing is also important if at all the device is fully compatible with the textile. Durability to washing has been performed by a number of researchers on developed textile electronics like sensors and antennas [127-129] due to its importance in textiles.

New developed textronic devices can be achieved from organic and inorganic materials in their advanced forms of microstructure or nanostructure [11, 42, 106].

If electronics have to be integrated into a textile garment, one is dealing with all possible electronic components like conductors, resistors, capacitors, transistors and displays. Electric conducting lines can be made by inserting electro conducting yarns into a fabric [9], or by suitable coating of conductive compounds on a non-conducting yarn [6,21,24,25,26]. The intrinsic conductive yarns can be made from materials like stainless steel, while coated conductive yarns can be from silver coated or copper coated conductive yarns. The electro conductive lines can also be obtained from hybrid yarns. Screen printing has also been successfully used to deposit conducting layers on a fabric [31, 47, 130]. However, textile being a flexible and porous material, one must take this into consideration while coating or printing conductive layers on it. Sometimes it is not easy to achieve a continuous conductive path from one layer of print or coat. The multiple layers may affect the textile material properties; increase stiffness or change in material strength.

Also the influence of the textile material on the electrical properties of developed products must be considered in the design stage [22,26].

It must be pointed out clearly that full integration into a fabric means that the electrical component is only made out of textile material and/or polymers embedded into the textile during the production process and not added as detachable in the final assembly of the garment. As a consequence, these components cannot be removed.

In this chapter we focus on testing the reliability and stability of the developed charge storage devices intended to supply power to the textile integrated electronic components and circuits. These developed devices so far can be described as “type I” capacitors (both the anode and the cathode are made of the same material – stainless steel filaments). PEDOT:PSS polymer is used as the "dielectric" or “electrolyte” material between the two yarn electrodes sewn into a textile substrate. The devices were charged and discharged severally until they failed. In other experiments, the charge storage devices were exposed to temperatures higher than room temperature while charging and discharging them. The effect on stored charge after dipping the devices in water for a few minutes was also studied.

4.2 Device fabrication

A three layered laminate of textile substrate (woven cotton/polyester) with the same specifications as used in chapter 3 was adopted. The electrodes were pure stainless steel filament yarns from Bekintex [131]. The two electrodes (negative and positive) were sewn at a close distance to each other (approximately 1.5 mm) into the fabric substrate. Therefore, there was no relative movement between the parts of the capacitor i.e. the solid electrolyte and the electrodes within the fabric, which would otherwise interfere with the working of the device. The upper surface of the fabric (except for a left out region of 10 mm by 6 mm including part of the electrodes) was made hydrophobic using a thermoplastic polyurethane (TPU) layer from Eurapex film company[95]. The TPU prevented the PEDOT:PSS from spreading too much on the fabric surface. The block design indicating clearly the dimensions details of the device is shown in Figure 4.1.

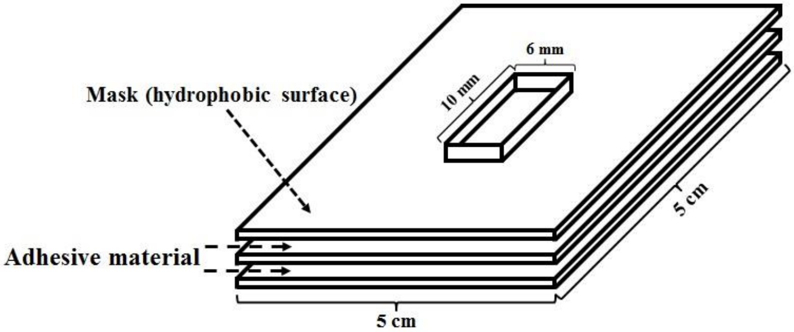


Figure 4.1 Textile substrate laminate showing the area where the electrolyte was applied

The PEDOT:PSS was applied on the foreseen area (10mm by 6mm) with a pipette while the fabric was in the oven. Each applied layer of PEDOT:PSS was left to dry in the oven for 15 minutes at temperatures of 90 - 100^{0}C, before applying the next layer. A total of 7 layers were drop coated in the defined region.

4.3 Cycling of the developed capacitor (repeated charge – discharge)

The charge storage device/capacitor was charged at a constant voltage of 1.5 V for 2 hours with the circuit shown schematically in Figure 4.2. After the two hours of charging elapsed, the switch was opened and the self-discharge of the PEDOT:PSS capacitor was recorded with a voltage metre having a high input resistance of 10 MΩ. Since each measurement lasted for several hours, the apparatus NI PXI (Figure 4.2) from National Instruments was used to carry out the operations automatically. The charge – discharge experiments were repeated severally until the device failed.

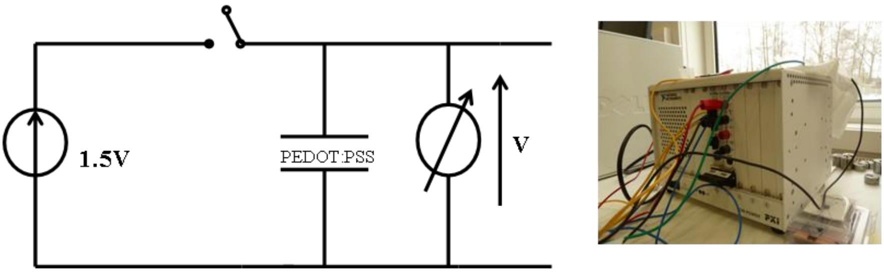


Figure 4.2 Charge - discharge circuit and the national instrument equipment used in this study

The charge storage device (capacitor) under experiment was not connected to any voltage for at least 10 hours before the next cycle was started. A day later, the second charging cycle began. The device was charged for 2 hours at 1.5 V, followed by measuring the second discharge characteristics for several hours. The third and the fourth cycle were performed in the same pattern. This procedure was repeated up to 18 times on the same device. The results of the first 14 cycles are shown in Figure 4.3. In these first 14 cycle, the voltage decay was more or less in the same trend and the device was still robust, at least within the first 10 000 seconds of each discharging. Voltage decay deteriorated only after the 14th cycle, hence affecting the level of charge stored in the device.

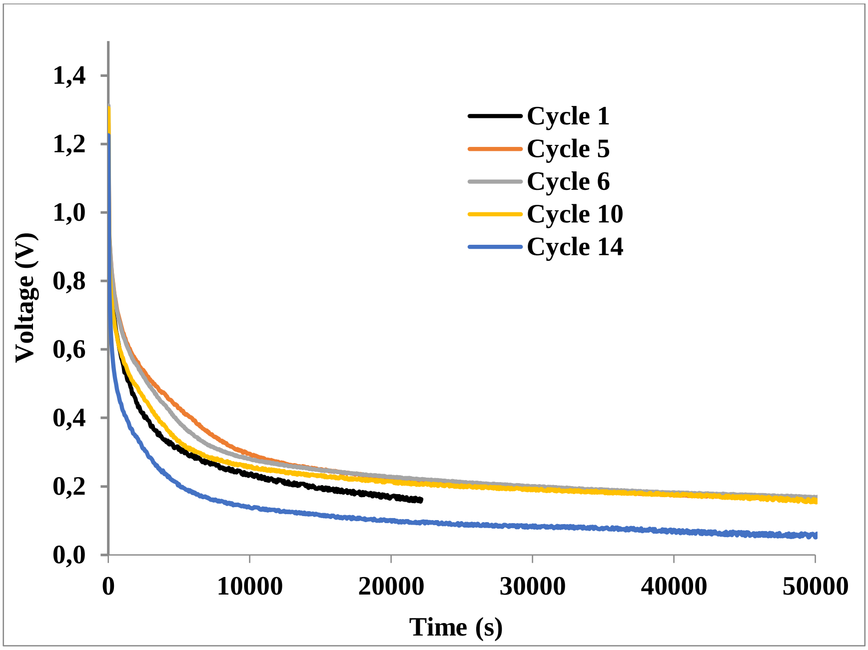


Figure 4.3 Voltage decay graphs of repeated charge-discharge on the developed charge storage device (Fatigue test measurements).

In Figure 4.3 the voltage decay of the cycles were drawn as a function of time for up to 50 000 s (about 14 hours). One remark that during the first 5 to 6 cycles as can be seen between 0 and 10 000 seconds, the output voltage is increasing, with increasing number of cycles, which means that the device is improving per each subsequent cycle. This could be due to the residual charge in the device from a subsequent previous charging. But when more cycles are applied, the device started yielding. This could also be attributed to the onset of the degradation of the electrolyte as the devices are not covered or protected against the ambient environment, whereas the charge - discharge experiments are conducted in the ambient environment of room humidity and temperature. Additionally, the chemical bonding between the PEDOT and PSS are weakened with the continuous cycling of the device, this is analogous to the report by Patra *et al*. [66] in their supercapacitors studies of electrochemically deposited PEDOT on stainless steel substrate. Their spectroscopic data reflects structural changes in PEDOT on extended cycling. They prepared the PEDOT:PSS electrodes in 0.1M H_2SO_4 in the presence of a surfactant sodium dodecyl sulphate which were found to yield higher specific capacitance than the electrodes prepared in neutral aqueous electrolyte. The specific capacitance values were initially as high as 250F/g, but there was a rapid decrease in the capacitance in the repeated charge - discharge cycle [66].

So long as there is structural or composition change in either of the components of the capacitor, the electrical properties of the capacitor is changed. This intern has a direct impact on the charge storage mechanism in the device.

A closer look at the characteristic of one single discharge graph from stainless steel filament yarn electrodes device in Figure 4.4 shows that the voltage drops rapidly in the beginning of the discharge process. But after some time (100 s) the voltage tends to be more stable at a value around 0.4 V for a rather long time (up to several hours). This can clearly be seen in the range of time between 0 and 10 000 seconds.

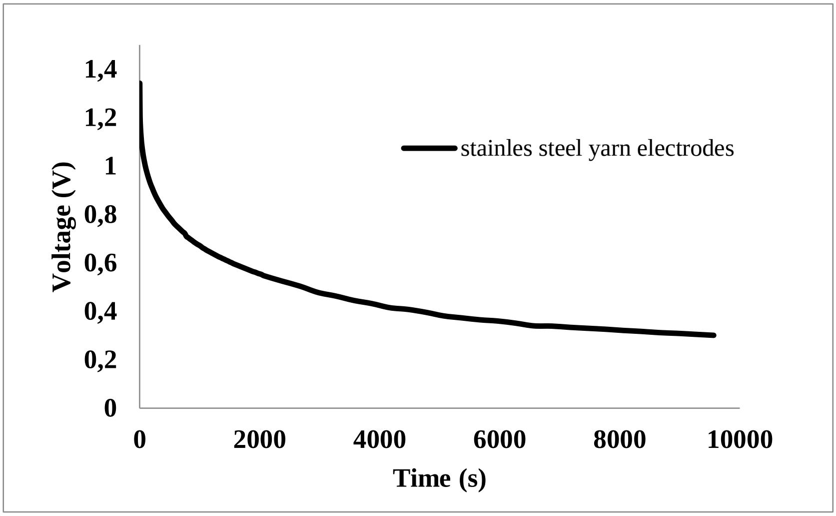


Figure 4.4 **Discharge characteristic (voltage decay) of single cycle.**

If one takes into account that a voltage of 0.4 V is rather small as compared to the initial charging voltage of 1.5 V, then the efficiency of our fabricated device is rather low. The efficiency in this case is calculated from the voltages. It is assumed that if the capacitor is charged at a constant voltage of 1.5 V, then when its fully charged it should be up to 1.5 V, however in our case the voltage drop is drastic in the beginning and there after slows down (see Figure 4.4). Therefore the voltage diminishes with time. Also the number of charging/discharging cycles is rather limited compared to the cycles that can be achieved by a conventional battery or capacitor (10 000cycles). But on the other hand, we are dealing with a device which is fully integrated into a textile fabric, where there are a lot of challenges to incorporate an electronic device by say coating or printing, compared to coating or printing conductive layers on solid materials like plastic films and boards. This is the price one has to pay to have a completely integrated electronic component into textiles.

The main purpose of this chapter was to investigate the stability and reliability of the repeated charge - discharge operations on PEDOT:PSS textile capacitors made with stainless steel filament yarn electrodes. Bhattacharya *et al*. reported that a similar device with silver coated polyamide filament yarn electrodes could be charged/discharged up to 4 times [37]. Accordingly our results presented in Figure 4.3 shows that devices equipped with pure stainless steel filament yarn electrodes can be charged/discharged up to 14 times without failure. Due to slow continuous discharge of the device, at least one day elapsed between each two consecutive cycles, to ensure that the cell is barely empty before the next cycle begins. Also Figure 4.3 clearly shows the onset of yielding of the cells after 5 to 6 cycles. From the first to the 5th cycles the output voltage is increasing with increasing number of cycles, but for the cycles there after the relatively decreasing voltage is clearly observed.

A clearer view of this phenomenon is shown in Figure 4.5, where the recorded output voltage is displayed as a function of the number of cycles N at several times after opening the switch *S* (t = 3 000 s, t = 6 000 s, t = 12 000 s, t = 18 000 s and t = 36 000 s).

Remark that t = 36 000 s corresponds to 10 hours of discharging time.

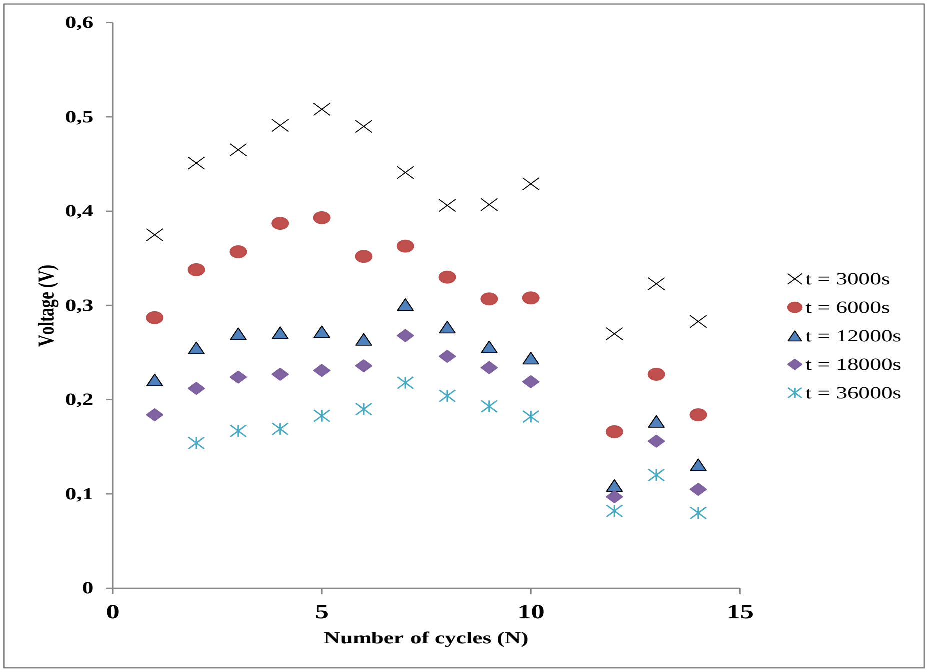


Figure 4.5 Graph showing discharge behaviour of the capacitors at specific times for different number of cycles (N) the timing starts just after opening the switch

Figure 4.5 shows the trend of voltage against the number of cycles for different times. It can be seen that there is a voltage drop after the 5th cycle.

One can roughly say that these capacitors can be used up to 10 - 15 cycles. This number is rather minimum and one might have the impression that these devices are inapplicable in practice. However, for wearable textiles which consume very little power and are not expected to last forever could be used with these devices. Additionally, a best combination array, of these capacitors, would give a reasonable voltage to support a textile electronic, although this research is limited to the study of a single capacitor not an array. Besides the study of PEDOT:PSS capacitors integrated into fabrics started very recently, and in most cases this material is reported for other areas of application like in electrodes for capacitors [19, 50, 52], interconnects [86], or for sensors [87] and only one other publication that has employed it as an electrolyte [37] in a textile battery. Therefore this topic is still in the initial phase of fundamental research.

Figure 4.5, shows the voltage values and trends for the number of cycles at a particular time. One might have the wrong impression that the measurements contain large errors because the curves are far from being smooth. This phenomena is entirely due to the (still unknown) physical mechanisms inside the PEDOT:PSS material. The voltage measurements of the devices were done with a digital instrument (National instrument) with a 3 digit accuracy. Such errors examined in this experiments are typical for reliability measurements [124, 125, 132].

Taking into account that the discharge curves were recorded with a voltage metre having a 10 MΩ input impedance, the current could be easily evaluated. A numerical integration gave the total charge. The ratio of this charge with respect to the applied voltage yields a capacitance value around 360 µF. By including additional resistors in parallel as reported in previous chapter, the internal series resistance of the PEDOT:PSS capacitor was found to be approximately 300 kΩ.

A typical problem related to PEDOT:PSS is that the electric conduction mechanism is still not well understood. As some authors claim it is still under debate [67, 111, 133] or in other words a lot of research has to be done to fully understand the fundamental phenomena happening in this material and the fabricated device. The charge and discharge is expected to involve cation transport [111] where migration or mass transport is expected to occur, hence some authors (Bhattacharya e*t al.*) report that by using silver coated yarn electrodes, electrolytic phenomena occur within the device, i.e. deposition of silver ions that moves from the anode electrode to the cathode electrode, this observation was done using SEM [37].

We observed that with silver coated yarn electrodes the output voltage was almost 50% lower than with the stainless steel yarn electrodes [20]. However, all the experiments involving different types of yarn electrodes proved that other phenomena like electrolysis cannot be excluded. Hence, one can start the discussion whether we are dealing with a capacitor or a battery or a hybrid. Obviously, when the conduction mechanism will be well understood, it will be easier to fabricate devices with better characteristics and performance.

4.4 Exposure of the charge storage device to water, and higher temperatures between 30^0C and 40^0C.

If the developed cell is to be used with clothing, it should withstand the laundry and care activities. It should also not be affected by slight increase in temperature, such that the smart garment with inbuilt batteries/capacitors could be used by sick persons with high fever or in personal protective clothing for persons working in the desert areas. The developed cells were made normally using PEDOT:PSS as electrolyte, and the stainless steel yarn electrodes in a textile substrate. PEDOT:PSS was drop coated on the yarns in the defined region of 10 mm by 6 mm over the yarn electrodes. Drop coating was followed by drying in the oven. No protective covering was used on the devices. It is normal that if the device is not protected in any way, when exposed to water the PEDOT:PSS will re-dissolve back to water (especially when there were no chemical changes in it during the drying period) since the drop coated PEDOT:PSS is from a water based dispersion. However, this diffusion process is a slow one, doesn't happen immediately, due to the surface tensions of the medias involved, so it will take some time before all the PEDOT:PSS goes back to the water solution. The loss of PEDOT:PSS electrolyte back to water and the water diluting the drop coated surface when the device is dipped in water affects the charge storage in the device.

4.4.1 Dipping the capacitor in water for 1 minute and for 5 minutes.

Capacitors were developed with pure stainless steel yarn electrodes and PEDOT:PSS electrolyte according to the procedure described earlier. The developed cell was then dipped in 200ml of demineralized water in a beaker for 1 minute, and dried for 1 hour in an oven between 43^0C – 48^0C. The device was then charged for 2 hours at 1.5 V and left to discharge overnight, where the voltage decay was measured.

Another device was also dipped in 200ml of water in a beaker for 5 minutes, then dried in the oven between 43^0C – 48^0C . The device was then charged at 1.5 V for 2 hours and discharged accordingly. Figure 5.6 shows the discharge characteristics of the devices after dipping them in demineralized water and drying.

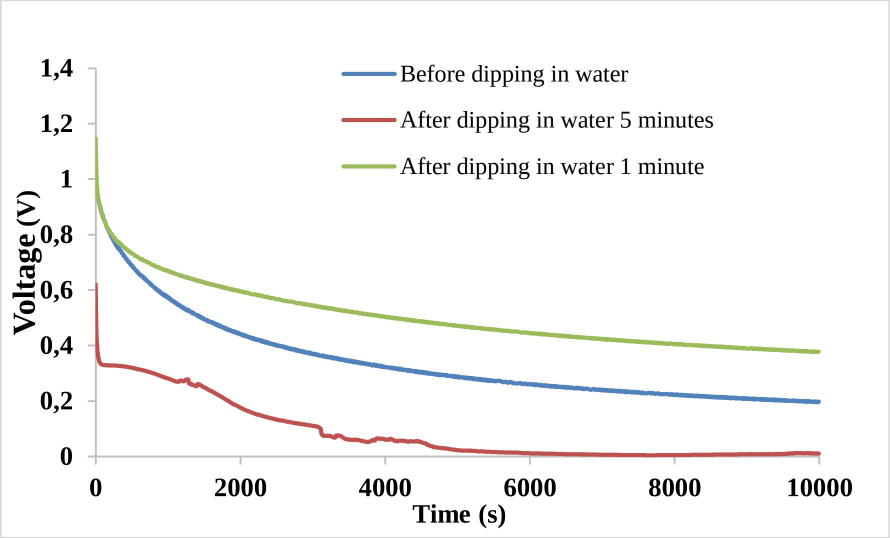


Figure 4.6 Effect of Dipping the cell in water

From Figure 4.6 it is noticed that dipping in water for one minute seemed to improve the device, but these results were not very reliable, since they were not consistent from one device to the other. However it is interesting to note that the increase in the level of accumulated charge in the device after dipping it in water for one minute then charging for 2 hours at 1.5V, happened in some devices. This leads back to the question of the working principle of the device. We could argue it, that for one minute dipping, only so little PEDOT:PSS is lost, and at the same time some little water is absorbed, by the hygroscopic PSS counterpart. This enhances the ionic conductivity in the device hence the observed results. When the device is dipped in water for 5 minutes, this time is long enough to loose more of the PEDOT:PSS electrolyte back to water. The water absorption into the device or the rate of loosing of the electrolyte (PEDOT:PSS) from the device to the water varied significantly from one device to the other, based on how the device interacted with the water. (some devices tends to float in water with the electrolyte part facing up, some down, and some were forced into the water, this varied the result). The device performance worsened, the longer it stayed in water. This can be explained by the fact that the PEDOT:PSS loading in the device is decreased, since some is lost back to the water. But the conclusion is that the devices needed a protective cover in case they are to be fitted into clothing that undergoes normal washing.

4.4.2 Exposure to higher temperatures

The effect of exposing the developed devices to temperatures of 30^{0}C, 35^{0}C and 40^{0}C were investigated and compared to the performance of the device under room temperature of 20^0C. The developed devices were kept inside the oven which was at temperatures of 30^0C, 35^0C and 40^0C respectively. The devices were then charged at 1.5 V for 2 hours while in the oven. After 2 hours of charging elapsed, the power source was disconnected and their voltage decay measurement were taken while they were still in the oven at the respective temperatures.

Figure 4.7 shows the discharge characteristics of the devices at 20^0C (room temperature), 30^0C, 35^0C and 40^0C. It can be observed that the heating effect lowers the level of charge storage in the devices especially if you look at the graphs in the region between 0 and 15 000 seconds. The voltage decay graphs for exposure to temperatures of 35^0 and 40^0C are very low and with errors. This implies that very little charge is stored in the device when they are exposed to this temperatures.

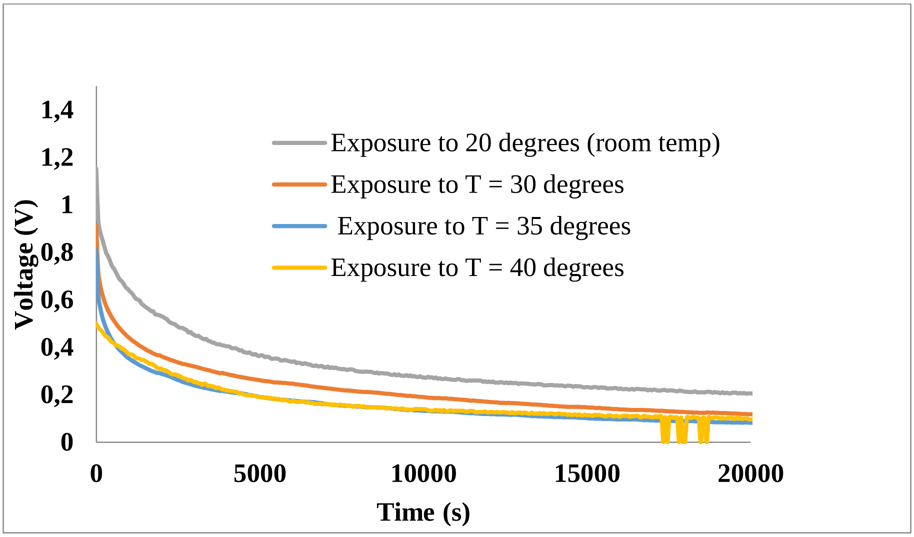


Figure 4.7 Effect of exposure to higher temperatures

4.5 Conclusion

Capacitors/charge storage devices well integrated into the textile structure that are small and light weight were made from PEDOT:PSS and pure stainless steel filament yarn electrodes. The devices show some robustness and could withstand up to 14 cycles of each 7 200 seconds charging at 1.5 V and discharging for a day. However, the amount of energy stored in the devices after charging is still very low due to the self-discharge. One can roughly say that these capacitors could be used up to 10-15 cycles, with no significant difference in the output voltage level for the first 14 cycles. This shows the limited life time of these developed capacitors compared to the conventional ones which can be charged thousands of times. If the devices were to be made more efficient, the self-discharge has to be improved. More research will be necessary in the future to find out how to overcome the self-discharge. It was also found that dipping the device in water had an adverse effect on the accumulated stored charge, therefore the cell cannot be subjected to water as it is, unless some covering/packaging is used on it to protect it. The developed devices performed poorly when exposed to temperatures above 30^0C.

5

Comparison of different types of PEDOT:PSS electrolyte in the “capattery”

In all the experiments performed in the previous chapters only one type of PEDOT:PSS obtained from Ossila company [55] was used to make the devices. There are several types of PEDOT:PSS, produced by different companies under different commercial brands. The differences in these types of PEDOT:PSS is in the formulation which contributes to the wide range of surface resistance of the product (90–700Ω/sq). and variation in other electrical, and physical properties. Possibilities of using other types of PEDOT:PSS as electrolyte in our devices was investigated. More interest was in the printed versions of PEDOT:PSS, so that instead of using the drop coating process we could use the screen printing process to increase the precision and uniformity of the electrolyte coating process. Electrolyte addition process to the developed capattery was to be screen printed rather than drop coated into the devices.

Two more brands of PEDOT:PSS aqueous dispersions were used differently to develop the devices by drop coating method, and two (2) different types of PEDOT:PSS, printable versions were used to develop the devices by screen printing. The textile based capacitors were made with silver coated PBO yarn electrodes in one type of device, and in another type with pure stainless steel filament yarn electrodes. A comparison of the performance of the different types of the PEDOT:PSS electrolyte in our devices has been done by voltage decay measurements. From the results, it is clear that the different types of the PEDOT:PSS have different strengths of charge storage.

It was discovered that NOT all the types of PEDOT:PSS could respond well as an electrolyte in the developed “capattery”. These additionally, increased the curiosity of finding out how exactly the devices were working. Since the debate on the working principle of these developed devices was not a clear cut whether it is a battery or a capacitor. The term “Capattery”, which is a terminology that has been used to describe a hybrid of battery and capacitor was adopted in these discussion to refer to the developed devices. The PEDOT:PSS from Ossila company emerged the best in charge storage in our devices. All the printed versions of the device could not store any charge. This show how this polymer can be manipulated to have a wide range of conductivity. We realized that our capacitors work best with a less conductive PEDOT:PSS with a conductivity range of (10^{-3} to 10^{-5}) S/cm. The performance of pure stainless steel filament yarns electrode still dominated the performance of silver coated PBO yarn electrodes for both the PEDOT:PSS electrolytes from Ossila company, and one type from Heraeus company (Clevious).

This chapter is based on the article "Comparison of commercial brands of PEDOT:PSS in electric “capattery” integrated in textile structure," *Mixed Design of Integrated Circuits and Systems (MIXDES), 2013 Proceedings of the 20th International Conference* , vol., no., pp.389,392, 20-22 June 2013

5.1 Introduction

Polyethylene dioxythiophene polystyrene sulphonate (PEDOT:PSS), used as electrolyte in our capattery is a conductive polymer which is widely investigated due to its unique electrical properties. This conjugated polymer from polythiophene family has unique electrical, electrochemical and optical properties that makes it have versatile electronic applications especially for smart textile systems. These types of polymers have been used to make transistors [98], batteries [67, 99, 134, 135] and supercapacitors [50, 136].

Conductive polymers are used to develop new versatile, flexible and porous electrode materials for batteries and supercapacitors. These materials have high theoretical capacities in the range of 100 -140 mAh/g [58, 59, 67]. PEDOT:PSS specifically has been used in combination with other materials to make the electrodes for the supercapacitors [67, 136]. It has also been used as an electrolyte material in rechargeable textile batteries [37, 53]. However, this polymer has been reported to have self-discharge, poor cycling stabilities and poor long term stability [54, 67]. Despite these characteristics a lot of investigations are performed to improve on the performance of this polymer in electric energy storage devices. Recently it was reported that the conductivity of PEDOT:PSS varies with the ratio of the two [69], and that the conductivity of this polymer can be enhanced using certain compounds like polyalcohols or high dielectric solvents [74, 82, 111].

Having involved unspecified PEDOT:PSS polymer in our device making process, from the results, it was not clear whether we were dealing with a capacitor or a battery or maybe something in between (hybrid). The term “capattery” was borrowed from some researchers who used it to refer to a device that is working as an in between battery and capacitor [19]. Further on, in this chapter we will use the word capacitor, device or capattery interchangeably.

5.2 Device fabrication and electrolyte application method

A three layered laminate of textile substrate was made from cotton/polyester fabric with the same specifications as described earlier in section 2.8. The yarn electrodes used were pure stainless steel filament yarns from Bekintex company [93] and silver coated PBO yarns from AmberStrand® company [90]. The upper surface of the fabric was made hydrophobic by using a thermoplastic polyurethane (TPU) layer from Epurex company [95] except for a left out region of 10mm by 6mm, where PEDOT:PSS was applied in layers. The TPU prevented the PEDOT:PSS from spreading too much on the fabric.

5.2.1 Drop coated electrolyte

Three brands/types of PEDOT:PSS aqueous dispersion (including the one that has been used in the previous experiments) were used as electrolyte to develop the two types of devices i.e. devices with stainless steel yarn electrodes and devices with silver coated PBO yarn electrodes. The PEDOT:PSS drop coated on the devices were from Ossila company (AI 4083) [55], from Heraeus company (Clevious P AI 4083) [57], and from Agfa company (ORGACON^{TM}) [56].

It was stated that AI 4083 is pure PEDOT:PSS in water, however the term ‘pure’ here is relative and has a high contribution in the conductivity of PEDOT:PSS, consequently in the development of these capacitors. We strongly believe that the water/solvents used in formulating the dispersion in addition, had an influence in the conductivity of the PEDOT:PSS in question. Even if it was the dispersion only in water like in the case of aqueous AI 4083, then the type of water used, makes a great difference in the conductivity of the polymer depending on whether the water is demineralized or normal or hard water. As a matter of fact we are talking of PEDOT:PSS dispersion in water where PEDOT:PSS is only 6% according to the data sheets of the product.

The PEDOT:PSS was drop coated using a pipette while the textile substrate was in the oven. The coatings were done in seven layers. Each layer of PEDOT:PSS was left to dry in the oven for 15 minutes at temperatures of 90^0 - 100^0C, before applying the next layer. This procedure was repeated with the three types of PEDOT:PSS aqueous brands on separate devices.

5.2.2 Screen printed electrolyte

The printable version of PEDOT:PSS were the Clevious SV3 and Clevious SV4 from Heraeus company [57].

NB: the S-grades which are printable versions contained not only PEDOT:PSS but also a binder and additives in a glycolic solvent to make the printing paste. By now we know that from the conductivity enhancement section 2.5.3, glycolic solvent is one of conductivity enhancing agent for PEDOT:PSS. Therefore when added to PEDOT:PSS the conductivity is increased significantly.

The laminated textile substrates with the yarn electrodes in them, and a hydrophobic cover on the surface were made in the department of textile Gent university, just as it was prepared for the devices that the electrolyte was applied by drop coating. The devices were then screen printed with the PEDOT:PSS electrolyte from the two printable versions in the department of functional material in Hasselt university where they have a well-established screen printing process and equipment, thanks to the collaboration between the two departments.

Since it was known that for the drop coated electrolyte, seven layers was more less enough, a test and measure method was employed to determine the number of screen printed layers, that would give the same thickness and resistance compared to the drop coated layers. The screen printing of the printable versions of PEDOT:PSS was done on plain cotton/polyester fabric in steps, of 1 layer screen print, 3 layers of screen print, 10, 20 and 50 layers and the resistances of the layers measured in each step. Some microscopy study of the layers and, preliminary conductivity tests of the printed layers were performed. The microscopic view of the device without the electrolyte, and the screen printed layers on the textile fabric are shown in Figure 5.1. The resistance of the PEDOT:PSS after 1 layer of screen print is in the order of GOhms, after 3 times a few MOhms and from 10 layers on around 100 kOhm.

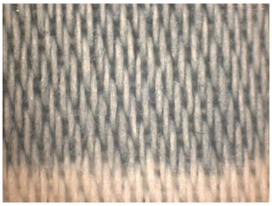
Clean textile substrate	1-layer print of PEDOT:PSS
	
3-layer print	10 layer Print
	
20 layer Print	50 layer print
	

Figure 5.1 Microscopy view of upper side of unprinted and printed PEDOT:PSS layers

It was found that the number of printed layers that would give a resistance equivalent to 300 kOhm (as estimated for the drop coated devices) was around 10 layers. Therefore the textile substrates with yarn electrodes in them were screen printed with 10 layers of PEDOT:PSS from the printable versions, to make similar devices with the drop coated ones.

5.3 Charge - discharge procedure of the developed capacitors

The PEDOT:PSS capacitors were charged one at a time at a constant voltage of 1.5 V for a sufficient long time (typically 2 hours). The switch *S* was closed (see Figure 5.2), and the capacitor was charged from the voltage source. After charging for 2 hours, the voltage source was disconnected by opening the switch and the charge stored in the capacitor was measured by the voltmeter. After opening the switch, the capacitor was discharged over the input resistance of the voltage metre (type 10 MΩ). The voltage decay measurements were carried out automatically with the NI PXI-1033 equipment of National Instruments.

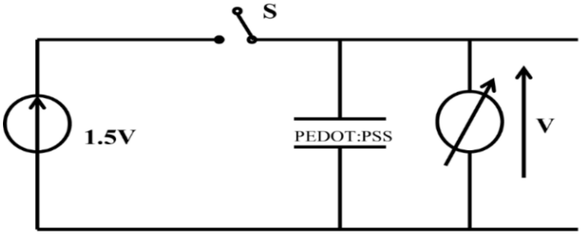


Figure 5.2 Charge-discharge circuit.

5.4 Experimental outcome

The results of different types of capacitors were compared according to their voltage decay characteristics. First, two types of yarn electrodes devices, i.e. pure stainless steel filament yarn electrodes, and silver coated yarn electrodes were drop coated with electrolyte separately for each of the three types of spin coat PEDOT:PSS. These three types of PEDOT:PSS were from Ossila, Agfa and Heraeus (Clevious) companies as stated earlier. Another type of printed electrolyte capacitors were produced from the two types of printable versions of PEDOT:PSS obtained from Clevious company.

The first comparison was performance between different types of yarn electrode devices using different types of drop coated PEDOT:PSS. Figure 5.3 shows the first comparison for drop coated PEDOT:PSS from Ossila company (AI 4083) which has also been presented earlier in Figure 3.10.

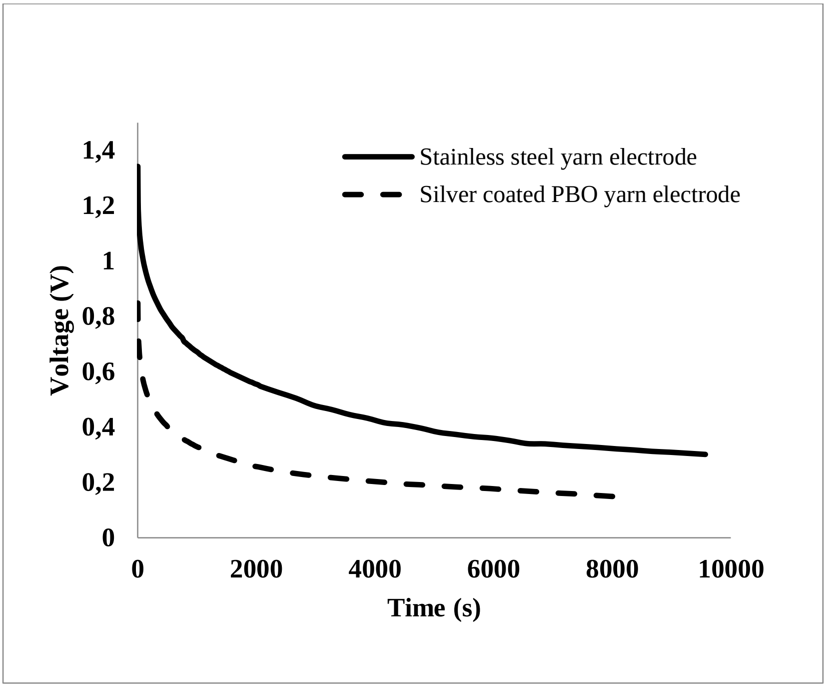


Figure 5.3 Comparison of voltage decay for the different types of devices using PEDOT:PSS from OSSILA company (AI 4083)

The stainless steel yarn electrodes were superior in their charge storage mechanism compared to silver coated yarn electrodes as already mentioned earlier, with spin coat type PEDOT:PSS from Ossila. Figure 5.3 shows typical discharge curves for the two types of capacitors. First of all one recognizes a steep decay in the beginning just after opening the switch for both types of yarn electrodes. After a few seconds say 4 000 seconds the output voltage has dropped from 1.5 to around 0.4 volts for stainless steel yarn electrodes, and dropped to lower values for silver coated yarn electrodes device (from 1.5 to 0.2). The capacitors display a longer relaxation time, in their voltage discharge characteristics.

Figure 5.4 shows the comparison of discharge characteristics of the two types of capacitors with PEDOT:PSS from Heraeus company (Clevious-spin coat type). The discharge characteristics are comparable to the previous ones with PEDOT:PSS from Ossila company. The voltage drops fast initially, then the discharge slows down after a couple of seconds. The capacitors with stainless steel yarn electrodes perform better than the ones with silver coated yarn electrodes using PEDOT:PSS electrolyte from Clevious too. However this type of PEDOT:PSS was weaker than the one from Ossila company for this application.

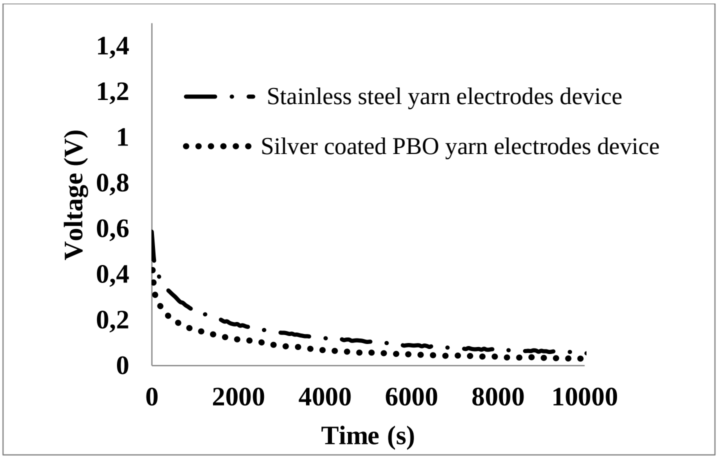


Figure 5.4 Discharge characteristics with Clevious PVP AI 4083; comparison of pure stainless steel filament yarn electrodes to silver coated yarn electrodes.

Generally, the output voltages of the Clevious PVP AI 4083 electrolyte is lower compared to the output voltages of devices with Ossila PEDOT:PSS. This could be associated with the polymer development method as already discussed earlier. One can clearly see that the two have same code number, but from our results the Ossila PEDOT:PSS was stronger as an electrolyte material in these developed capacitors compared to the Clevious PVP AI 4083.

A third experiment was made with devices drop coated with PEDOT:PSS from Agfa company (ORGACON^{TM}). With these devices, the discharge was very fast and immediate, that could not be observed in the seconds scale. Again with this polymer version we highly suspect that its conductivity in pure state was higher than the Ossila (AI 4083). If we may refer to Stocker *et al.*[69] research results (see Table 5.1), we can see that the conductivity of PEDOT:PSS can be varied widely based on the PEDOT to PSS ratio. Additionally, depending on whether the conductivity enhancers are used in production process or not. However from the manufacturers not all of them give the details of the product in terms of the PEDOT:PSS ratio used or the conductivity enhancers used.

Table 5.1 Applications of PEDOT:PSS based on PEDOT to PSS ratio

PEDOT:PSS Ratio	Solid content	Conductivity S cm^{-1}	Application
1:2.5	1.3	1	Antistatics
1:6	1.5	10^{-3}	OLEDS
1:20	3	10^{-5}	Passive matrix display

Comparison of the performance of the 3 types of spin coat versions of PEDOT:PSS electrolytes is shown in Figure 5.5. Only stainless steel yarn electrodes devices were used in these comparison.

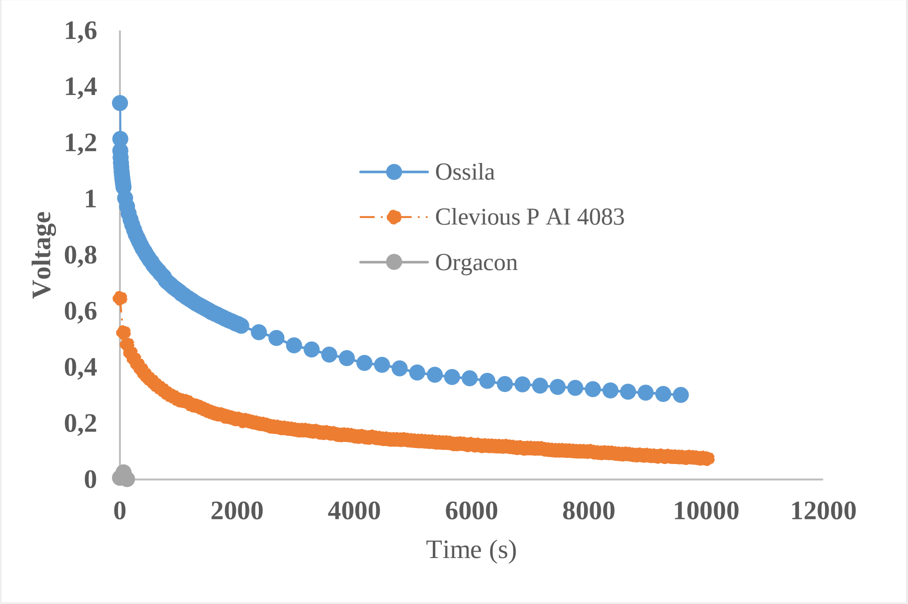


Figure 5.5 Voltage decay for 3 different types of drop coated PEDOT:PSS versions using stainless steel yarn electrodes. Charging time 2 hours at 1.5V.

From Figure 5.5 it is clearly seen that capacitor made with PEDOT:PSS from Agfa company (ORGACON^{TM}) could barely store any charge, its voltage decay graph could not be observed in this time scale, while the capacitors made with PEDOT:PSS from Ossila company stored more charge compared to the ones with Clevious PVP AI 4083 PEDOT:PSS. These shows that Ossila PEDOT:PSS was with better charge accumulation in our developed devices. We discovered that our devices worked best with PEDOT:PSS with a lower conductivity in the range of (10^{-3} to 10^{-5}) S/cm. From the result it seems that PEDOT:PSS (AI 4083) had a conductivity in this range, and the other types of PEDOT:PSS had different conductivity.

Screen printed capacitors made with stainless steel filament yarn electrodes and with PEDOT:PSS from Clevious; Clevious SV3 and Clevious SV4, were also charged for 2 hours and left to discharge. Apparently, they could not store charge, voltage decay results from this devices are not shown.

5.5 Electrical and chemical properties of the different types of PEDOT:PSS electrolyte used in the developed capacitors

The differences in the charge storage behaviour for the different types of PEDOT:PSS capacitors has been associated to the PEDOT to PSS ratio differences in the brands experimented and also to the non/addition of conductivity enhancing agents into the PEDOT:PSS as per our speculations. We made more analysis of the existing differences of the experimented brands of the electrolyte in terms of their chemical composition, physical, and electrical properties. This was to confirm if there could be additional elements that contributed to the charge storage mechanism in the different formulations of PEDOT:PSS. From literature search, it was found that PEDOT:PSS conductivity varies with the ratio of PEDOT to PSS [69] and also that conductivity enhancing agents [74, 81] could bring great difference in the performance of the PEDOT:PSS .

PEDOT:PSS is a common material produced by many companies for various applications as stated earlier. It is produced by several companies in Europe and America. A lot of research is currently being conducted to enhance these polymer conductivity. This makes a whole range of these product available in the market, in fact some companies have a series of the improved versions of the polymer, of which each version targets a given application and mostly with increased conductivity.

With this knowledge the 5 different types of PEDOT:PSS used in this research were randomly selected and compared in terms of their parametric properties as given in Table 5.2. However, this comparison was with difficulties because the manufacturing companies did not provide most of the details of the PEDOT:PSS formulations.

The properties of the PEDOT:PSS brands are presented according to their application technology in our devices, i.e. drop coated – Ossila (AI 4083), Clevious (PVP AI 4083) and ORGACON^{TM} and the printed versions Clevious (SV3 and SV4).

Table 5.2 Conductivity related parameters for the 5 types of PEDOT:PSS formulations as given by the manufactures

	Ossila PEDOT:PSS 4083	**Clevious PVP AI 4083**	**ORGACON^{TM} ICP 1050**	**Clevious SV3**	**Clevious SV4**
	Drop coated			Printed	
Sodium content (ppm)		400	100		
Sulphate content (ppm)		40	80		
Composition	94% water				
Solid content (%)		1,3-1,7			
Resistivity Ωcm		500 - 5000			
Surface resistance Ω/sq			90	700	400
Viscocity		5 to 12	30 - 100 mPas	15 - 60 (dpas)	15 - 60 (dpas)
Form	Liquid	Liquid	Liquid		
PEDOT:PSS ratio		1:06			
pH at T20 ^{0}C	1,5-2,5	1,2 -2,2	1,5 - 2,5		
Boiling point (^{0}C)	100	100			
	Brief heating up to 50^{0}C has no adverse effect on product property.- Heraeus				

From Table 5.2 the available parametric information from the data sheets as provided by the manufacturers is compared. Not all data for the PEDOT:PSS brands were availed by their manufactures in the product data sheets. Our main concern from the data was first the difference in the surface resistance and resistivity which was widely varying across the table, secondly the PEDOT to PSS ratio, but this information was available only for Clevious PVP AI 4083. Sodium and sulphate components in the polymer dispersion is clearly different between ORGACON^{TM} and Clevious PVP AI 4083. The resistance of the products in terms of Ω/sq varies greatly with ORGACON^{TM} ICP 1050 having the least.

The values presented above are for the aqueous state of PEDOT:PSS. For a better comparison of the processed layers of PEDOT:PSS in our devices, it was important to derive a uniform unit of resistance for all the brands and compare these values for the different types of PEDOT:PSS. We assumed that the deposited layer of PEDOT:PSS (drop coated and screen printed) on the textile substrate with the conductive yarns already inserted had a thickness of t_s = 10 µm. The square resistance is then given by Equation 7.

$$\boldsymbol{R_{\square}} = \frac{\rho}{\boldsymbol{t_s}} \qquad \textbf{Equation 7}$$

Where ρ is the resistivity of the material.

Using ρ = 500-5000 Ωcm for Clevious spin coat PEDOT:PSS, we obtain a square resistance in the range of $R_{\square}$ = 0.5 - 5 MΩ which is much higher than the value of 90 Ω given by ORGACON^{TM}.

The same conclusion still holds if we would use another value for the thickness t_s. It is also remarkable that the pH of these materials is almost identical in the acidic range of 1.2 - 2.2 versus 1.5 - 2.5 (given by the suppliers). The viscosity of the provided material is clearly different from one brand of PEDOT:PSS to the other and especially for the screen printed versions from the drop coated ones. This has an influence on the number of layers deposited on the substrate to make the capacitors. For the more viscous PEDOT:PSS (ORGACON^{TM}) roughly 5 layers of the drop coats was equivalent to the seven layers of the less viscous brands (Ossila) and this number of layers is equivalent in resistance to 10 layers of the screen printed layers. The number of layers had an influence on the bulk resistance but probably not on the working principle of the capacitor.

Prior to this comparison, the conductivity of the aqueous dispersions of the drop coated PEDOT:PSS were measured physically in-house at room humidity and temperature using CDM 210 conductivity metre. The values are given in (mS/cm), see Table 5.3

Table 5.3 Conductivity measurements of aqueous PEDOT:PSS

Average values	**Ossila AI 4083**	**Clevious PV AI 4083**	**Orgacon ICP 1050**
Conductivity mS/cm	8.0	7.2	5.93
Temperature ^{0}*C*	20.2	19.2	19.8
Relative Humidity %	36.6	32	37

From these results it was noted that the conductivity in aqueous solution showed that ORGACON^{TM} had a lower conductivity compared to Clevious PVP AI 4083 and Ossila AI 4083 . But again here we are dealing with conductivity in aqueous solution where it´s reported that the PEODT:PSS component is about 6%. Therefore the conductivity in this case is additionally dependent on the type of water used, and the solvents present.

5.6 Discussion

The main cause of the differences in the performance of these types of PEDOT:PSS polymer in the developed capacitors, in our opinion would be in the composition of the polymer dispersion, and the ratio of PEDOT to PSS which is kept secret by the companies involved. Not all the information about this polymer which is key in determining our results were disclosed by the manufacturers. In one recent research it was stated that the conductivity of PEDOT:PSS varies with the ratio between these two polymers [69]. If the ratios of PEDOT to PSS are different between the 5 types of PEDOT:PSS, then this could be a major contributor to the differences in their performance in the developed capacitors.

Apparently all the screen printed versions of the device did not store charge. However, this was not investigated further. Also devices made with PEDOT:PSS from ORGACON^{TM} that was drop coated could not store any charge. The output voltage dropped immediately to zero after opening the switch of the charge – discharge circuit. The equipment of National Instruments was not fast enough to detect any voltage in the range of milliseconds of these devices made with PEDOT:PSS from Agfa company, as a consequence we discontinue use of this material as an electrolyte in further research in the development of the capacitors. This result was a big challenge for the research to advance, and it led to the investigation of the PEDOT:PSS material itself. Anyhow we decided to continue with PEDOT:PSS from Ossila, and stainless steel yarn electrodes, and focused on exploring the device in the later chapters.

5.7 PEDOT:PSS material investigation

From the results obtained with these different types of PEDOT:PSS, it is clear that this polymer has a lot of variations in its characteristics especially if it contains other additives for enhancing conductivity. PEDOT:PSS is a combination of two organic molecules: polyethylenedioxythiophene and polystyrenesulphonate, but some of the formulations may contain other additional components. It must be pointed out that the basic physics of the electric conduction mechanism is not yet well understood. Some authors wrote that it is still under debate [137] [81]. The structure of this PEDOT:PSS polymer is shown in Figure 5.6.

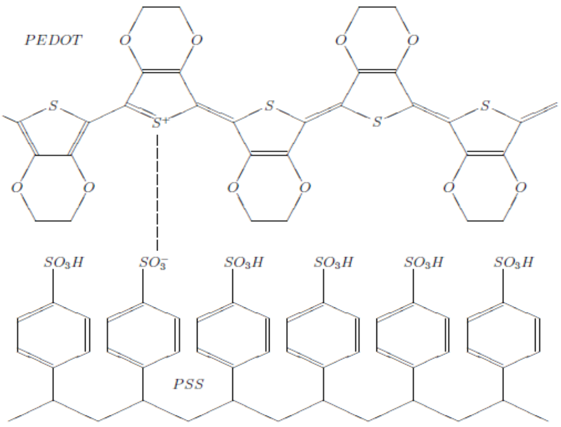


Figure 5.6 PEDOT and PSS molecules interaction via charge transfer

In an attempt to explain the working principles of charge storage mechanism at molecule level, the process was related to the structure of PEDOT:PSS see Figure 5.6. The PEDOT molecule can loose one or more electrons whereas the PSS receives those electrons. The PEDOT has several S^+ (positive) ions whereas a PSS molecule will have then one or more $SO_3{}^-$ (negative) ions. If an electron jumps from PEDOT to the PSS as shown by the dotted line Figure 5.6, electric conduction should become possible, where the electron is captured by SO_3 group making the PSS negative and the PEDOT counterpart positive. It is assumed that charging induces this electron jump process, and the process also depends on the type of electrode material used.

Under influence of an externally applied electrical field the charged PEDOT and PSS polymer chains will move in opposite directions so that the material will be electrically polarised and the capacitor becomes charged (see explanation in chapter 3.5 Proposed charge storage mechanisms in the developed cells). After removal of the applied electrical field the ions will move back to their original position so that the material loses its polarisation.

The conductivity of PEDOT:PSS highly depends on the polymerization process (chemical polymerization or electrical polymerization) [119] [80], purity of the product, the ratio between PEDOT and PSS, and the application process among others.

A capacitive process occurs in the electro-conductive polymer coating (PEDOT:PSS) on the textiles associated with movement of charge carriers to the interface between the polymer and the yarn electrodes.

The behaviour of the charge storage varies with the type of material interface, i.e. steel/PEDOT:PSS or silver/PEDOT:PSS. SEM-EDX imaging and FTIR spectroscopy in some literature has confirmed ion transport and redox reversibility in PEDOT:PSS

[81, 120]. However the type of material of yarn electrode also contributes to the rate of the ion transport. Over-oxidation of this polymer causes irreversible deactivation of the polymeric coat, and hence the mechanical breakdown of the devices.

5.8 Conclusion

Different brands (5) of PEDOT:PSS were compared for use in making textile-based capacitors. From the analysis, it is clear that the five different types of PEDOT:PSS have different performances in our developed devices. A closer look at the polymer dispersion composition and the electrical properties indicate that the parameters are varying from one brand to the other. The best product for our application so far was PEDOT:PSS from Ossila AI 4083 as it could store more charge in the developed devices.

Since the charge storage from the results presented varied between different types of PEDOT:PSS, it means that there could be some other additives in this PEDOT:PSS mixes and in different proportions that caused the variations. Also the ratios of PEDOT to PSS which is barely mentioned in the data sheets by the manufacturers would bring this variations. It is possible that the printable versions could not store charge, because this mechanism of charge storage is hindered by the presence of binders, but this is not a conclusive remark.

The performance of pure stainless steel filament yarns in the developed devices dominates the performance of silver coated PBO yarn electrodes devices.

The results motivate the making of a functional textile-based capacitor integrated within the textile structure using stainless steel filament yarn electrodes with PEDOT:PSS from Ossila company.

6

Influence of yarn electrode diameter on the voltage discharge of PEDOT:PSS capacitors

Textile based capacitors were produced from polyethylene dioxythiophene: polystyrene sulphonate (PEDOT:PSS) from Ossila company in combination with pure stainless steel yarn electrodes. The aim of this chapter was to try replace the thick yarn electrodes which were sewn into the device with difficulty, with thin yarn electrodes which would be easier to insert into the device assembly. Three different sizes of yarn electrodes with different yarn diameters were used to produce three different capacitors. The developed capacitors were characterized by their voltage decay (discharge characteristics) measurements. The differences obtained in the results were investigated. Our initial hypothesis was that the voltage decay would be dependent on the yarn resistance. The three sizes of yarn electrodes referred to as thin, medium and thick had yarn diameters approximately between 100µm to 400 µm. It was difficult to explain the results initially, since the charge storage mechanism was still under discussion, and eventually it was found out that the voltage discharge was not dependent on the yarn electrode resistance but on the yarn diameter. The yarn electrodes were from the same material stainless steel filament yarns.

We eventually used the yarn diameters to determine the electric field strength around each yarn electrode within the capacitors. We found a mathematical relationship between the electric field strength around the yarn electrode and its diameter. The electric field around the yarn electrode is stronger for the thin yarn compared to the medium and the thick yarns. This resulted to a faster voltage decay with the thin yarn electrode. This means that in our capacitor concept we could retain less charge with thin yarn electrodes compared to the capacitors with medium and thick yarn electrodes. Generally overcoming of self-discharge of the PEDOT:PSS capacitors would bring better results.

This chapter is based on the publication Odhiambo, S. A.; De Mey, G.; Hertleer C.; and Van Langenhove L., “Influence of Yarn Electrode Diameter on the Discharge Characteristics of PEDOT:PSS Textile Capacitors” Under review.

6.1 Introduction

There is a continuous improvement in the development of smart textile systems, which originated from incorporating rigid electronic components [103] into textiles (where functional components are non-textile), to transforming the components into fully textile themselves [47, 113, 138]. The evolution is driven by the demand of developing new inexpensive, flexible, light weight and non-toxic electronic devices [67, 134, 139] which are compatible with textiles, for smart textile applications and wearable electronics.

Intrinsically conductive polymers such as polyaniline, polypyrrole and polythiophenes, in combination with conductive yarns have been used to make textronics [98, 136, 140]. However, it has been reported that initially the conductive polymers compared to metal experience self-discharge, poor cycling stabilities and poor long term stability [67]. These characteristics are continuously being improved by material scientists, for example by introducing electron withdrawing groups into the polymer matrix [67]. Conductive polymers have also been used for the fabrication of battery and capacitor electrodes, typically for the cathode. For the anode, traditional metal electrodes are preferred [99] because they have higher specific energy than conductive polymers.

In this research PEDOT:PSS was used as an electrolyte to make an electric capacitor well integrated into a textile grid and which has pure stainless steel filament yarns as electrodes. The aim of this chapter was to try replace the thick yarn electrodes which were sewn in with difficulty, with thin yarn electrodes which would be easier to insert into the device assembly and with less short circuits between the electrodes compared to the thick yarn electrodes. Therefore three different yarn electrodes (thin, medium, thick) of pure stainless steel filament yarns were used to test the influence of the yarn electrode thickness on the performance of the device. The yarn electrodes were specified by their yarn count (in Tex), yarn diameter (in µm), number of filaments per yarn, number of plies and linear resistance (Ω/m).

6.2 Devices preparation

To make each of the capacitors with different size of yarn electrode diameter, a three layered laminate of woven cotton/polyester with specifications as given in section 2.7 was used [53]. The yarn electrodes were made from stainless steel yarn from Bekintex [93]. The PEDOT:PSS chosen for this experiment was the one from Ossila company (AI 4083). The thermoplastic polyurethane layer (TPU) used originated from Epurex [95]. The textile fabric that was readily available in the department was made of cotton/polyester material. The device was fabricated in the same way as it has been done, but in this case only two yarn electrodes per device (positive and negative) were used instead of three. This far, with the mastery of device development, it was realized that two yarn electrodes well inserted in the devices could also yield good results. Three electrodes were used initially in case one contact would fail. However in all the cases weather two electrode or three electrodes, only two connections were considered i.e. positive electrode and negative electrode.

To produce the three types of capacitors, thin, medium and thick stainless steel filament yarns with different yarn count and structure were used as yarn electrodes. The two electrodes in each device (see Fig. 1) contained only one type of yarn electrode. PEDOT:PSS, which is supplied as a dispersion, was coated onto the yarn electrodes. The upper surface of the capacitor was made hydrophobic using a TPU layer, except for a left out region of 10 mm by 6 mm. The PEDOT:PSS was applied on this foreseen area with a syringe in layers, while the fabric was in the oven. Each layer of PEDOT: PSS was left to dry in the oven for 15 minutes at temperatures of 90-100^{0}C, before applying the next layer. The TPU prevented the PEDOT:PSS from spreading too much on the fabric and instead be contained in the 6mm by 10mm region. A real and schematic view of the capacitor is shown in Figure 6.1.

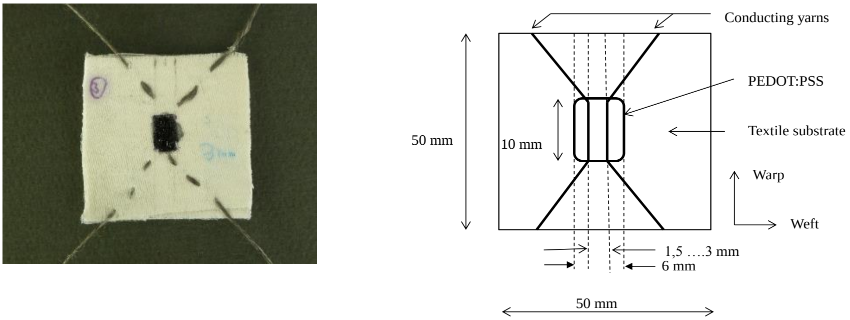


Figure 6.1 Real and schematic view of the PEDOT:PSS capacitor

The specifications of the three sizes of pure stainless steel filament yarns are shown in Table 6.1. The yarns are classified and named by the manufacturer according to their specifications in terms of filament diameter, number of plies, number of filaments per ply and the twist direction. Nevertheless we simplified them to thin, medium and thick yarn electrodes, i.e.

Bekinox VN 14/1x90/100Z/316L (thin),

Bekinox VN 12/1x275/100Z (medium) and

Bekinox VN 12/4x275/100S (thick).

The medium and the thick yarn electrodes, have filament diameter of 12 μm, but different number of total filaments and number of plies (one and four respectively). They also have different types of twist direction (*Z* and *S* respectively). The third type of yarn (thin) has 14 μm filament diameter, and no plies, just 90 filaments bundled together.

Table 6.1 Stainless steel yarn filament specifications

Type	Filament diameter (μm)	No. of filaments	Yarn count (Tex)	Linear resistance (Ω/m)
VN 14/1x90/100Z316L (**Thin**)	14 μm	90	110	70
VN12/1x275/100Z/316L (**Medium**)	12μm	275	250	25
VN12/4x275/100Z/316L (**Thick**)	12μm	1100	1000	7

All the yarn electrodes were from the same supplier but of different sizes and they will be referred by their diameter size as thin, medium and thick yarn electrodes. Since all the yarn electrodes have different number of filaments, obviously the more number of filaments they have, the thicker the yarn, so from the table it can be seen that the yarn linear resistance is inversely proportional to the yarn size.

6.3 Charging and discharging procedure

The fabricated PEDOT:PSS capacitors were charged at a constant voltage of 1.5 V for 2 hours according to the electric circuit shown schematically in Figure 6.2. After charging, the switch was opened and the self-discharge of the capacitor was recorded with a voltage metre having a high input resistance of 10 MΩ. Since each measurement lasted for several hours, the apparatus NI PXI from National Instruments was used to carry out the charge - discharge procedure automatically. The *NI PXI 1033* is a chassis equipped with several voltage generators, a digital voltage metre and a computer interface. A relay was used as the switch of the circuit which was controlled by one of the voltage generators. Dedicated software running on *LabVIEW* was written to carry out all measurements automatically.

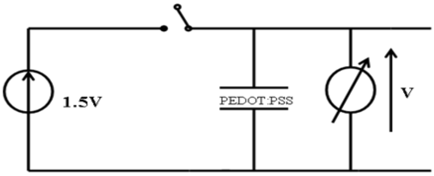


Figure 6.2 Schematic layout of the charging circuit

6.4 Discharge characteristics graphs

Some of the voltage decay graphs (discharge characteristics) from the different sizes of yarn electrodes are shown in Figure 6.3. The voltage decay is a function of time, V(t). The graph of thin yarn is not a smooth curve, but a zigzag curve; this can be associated with the way it dissipate the accumulated charge after the charging process. The thin yarn electrodes shows faster decay than the medium and thick yarn electrodes. All discharge curves are quite fast in the beginning and slows down after a long time as it has been described in our publications [53, 54, 141]. Such a discharge curve is totally different from the discharge curve of a normal electric capacitor presented in section 1.4.1 Charge – discharge of a capacitor. The latter gives rise to an exponential discharge curve.

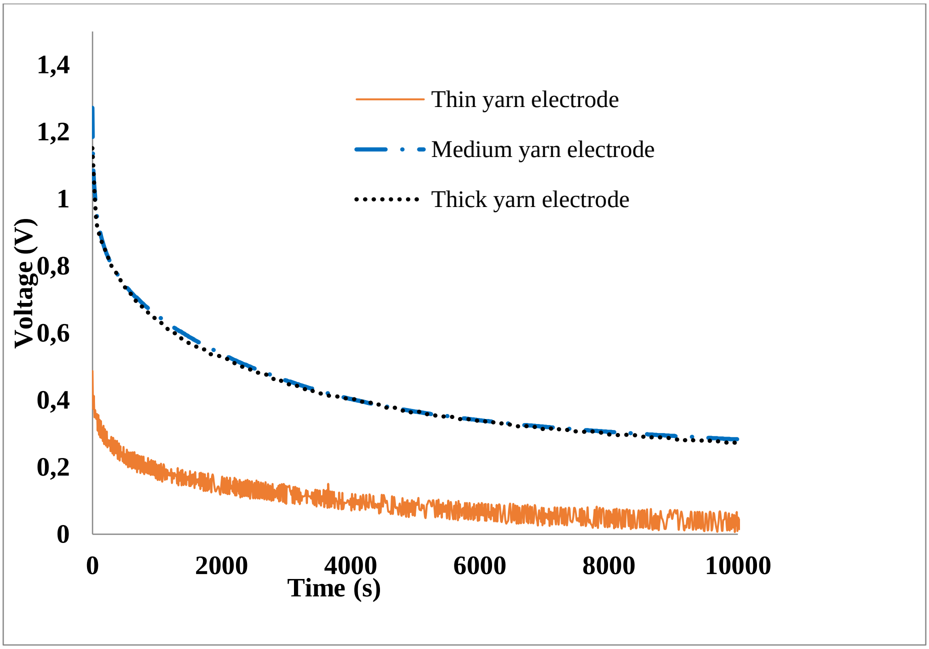


Figure 6.3 Comparison of Voltage decay of the different diameters of yarn electrodes

It is observed clearly that the thin yarn electrodes showed fastest decay compared to the two other i.e. medium and thick yarn electrodes. Referring to Table 6.1, the medium and thick yarn electrodes are made from filaments of the same diameter, the difference is in the number of filaments bundled together to form the yarn. The thin yarn electrode is made of filaments of larger diameter, however the number of filaments bundled together are fewer. They are barely twisted together.

It is clear that the series resistance of the yarn electrodes cannot be responsible for the observed phenomena. The total length of the yarns during the measurements was no more than 10 *cm* which gives rise to a series resistance of 7 Ω maximum. The time constants observed in Figure 6.3 are in the order of hours, which in combination with a resistor of only 7 Ω would require a huge capacitance value impossible to realize with the small capacitor configuration we are dealing with. The only parameter which remains to be investigated, is the yarn diameter. It is shown theoretically in this section, that the thinner the yarn electrode the stronger the electric field will be on its surface. This will explain the phenomena shown Figure 6.3.

In this work three types of yarns, all made from pure stainless steel material, were used. The values of their diameters were not provided by the supplier. So we determined them ourselves.

The thin yarn electrode is made from *90* filaments, each having a diameter of $d = 14 \mu m$. If we assume that each filament is a perfect cylinder with diameter $d = 14 \mu m$, the theoretical diameter D_{th} of the yarn is then $6/\surd 3\, \pi = 1.102$ times the area of the filaments. If N filaments are used, we get the theoretical diameter as determined by Equation 8.

$$\frac{\pi D_{th}}{4} = N\frac{\pi d^2}{4}\,\frac{6}{\sqrt{3}\pi} = \frac{6Nd^2}{\sqrt{3}} \qquad \text{or} \qquad D_{th} = \sqrt{\frac{6N}{\sqrt{3}}}\,d \qquad \textbf{Equation 8}$$

For the thin yarn electrode with $d = 14 \mu m$ and $N=90$ we get $D_{th} = 139 \mu m$. A similar analysis for the medium yarn electrode, with $d = 12 \mu m$ and $N = 275$, we get that $D_{th} = 208 \mu m$. The thick yarn electrode is composed of four plies, same as four of the medium yarn electrodes plied together, so that $N = 4 \times 275 =1100$ and $D_{th} = 417 \mu m$. The three theoretical diameters of the yarn electrodes are listed in Table 6.2.

Another method of determining the yarn diameter that was used is based on the weight per unit length of a yarn (Tex or dTex). The Tex values are given by the supplier see Table 6.2. Equation 9 was used to find the yarn diameter:

$$D_{tex} = \sqrt{4 * 10^{-6}\, dtex}\, \pi\rho \quad \text{in cm} \qquad \textbf{Equation 9}$$

where ρ is the density of the material to be expressed in g/cm³. For stainless steel material the density is $\rho = 7.85\ g/cm^3$[10], with the *dtex* values given by the supplier we obtained the theoretical diameters of $133 \mu m$, $201 \mu m$ and $402 \mu m$, which are very close to the theoretical diameter values $139 \mu m$, $208 \mu m$ and $417 \mu m$ obtained by using Equation 8. An overview of all the determined diameters is shown in Table 6.2.

Table 6.2 Comparison between the theoretical diameter D_{th}, the diameter D_{tex} obtained from dtex values and the measured diameter D_{meas} for the yarn electrodes.

Yarn electrode	Filament Ø	Tex (Linear density)	Number of filaments	**D_{th}**	**D_{tex}**	**D_{meas}**
	µm	*g/1000m*		*µm*	*µm*	*µm*
Thin	14	110	90	**139**	**133**	**211±48**
Medium	12	250	275	**208**	**201**	**312.5±43.5**
Thick	12	1000	1100	**417**	**402**	**762±61**

Both equations Equation 8 and Equation 9 assume the most dense arrangement of cylinders (filaments), hence the calculated diameters will always be lower values, assuming a close packing of filaments. To confirm this, the actual measurements were carried out to determine the real diameter of the yarns used. Images of the yarns were made using a stereoscope microscope, these are shown in Figure 6.4. The diameters were measured from the images at several sections. These several measurements (of which the average was taken) were necessary because one can easily observe that the yarn diameter is not constant along the twisted yarns, the porosity also is not constant within the yarn length, this changes during handling. In Table 6.2 the average values of the measured diameters and their range (+/-) are given. One remark is obvious: the measured diameters (D_{meas}) are much larger than the calculated ones (D_{th} and D_{tex}).

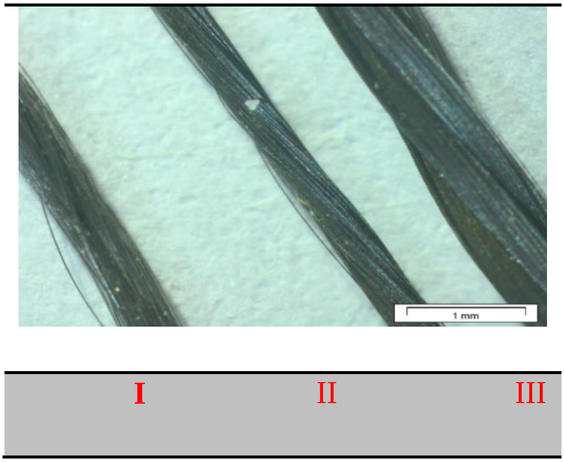


Figure 6.4 Images of the three stainless steel yarn electrodes *I - thin, II-medium* and *III-thick*

6.5 Theoretical model of the device design and discussion

The experimental results clearly show that the thin yarn electrode had fastest voltage discharge whereas the two other yarn electrodes, medium and thick had comparable discharge characteristics. The question is then, what parameter could be responsible for this phenomenon?

Roughly speaking, the diameters of the yarn electrodes; thin, medium and thick are *100, 200* and *400 µm*. So we have to find a parameter which has a different value for the *100 µm* yarn electrode diameter. At the same time this parameter should also be almost constant for yarn electrode of *200 µm* and *400 µm*. It will be shown here that the electric field strength at the electrode surface satisfies this condition.

In order to set up a simple mathematical model, a cross section (z - section) of the capacitor is represented by the two dimensional geometry shown in Figure 6.5.

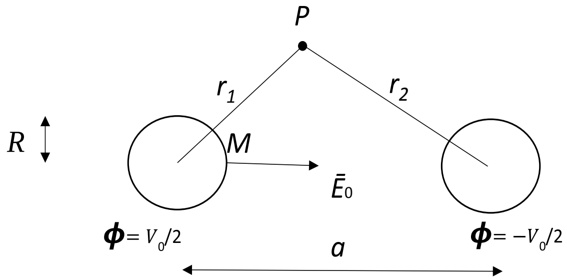


Figure 6.5 Cross section of the capacitor, the two yarns are at potentials $\Phi = V_0/2$ and $\Phi = -V_0/2$

Figure 6.5 roughly represent how the two yarn electrodes are situated in the PEDOT:PSS capacitor. The yarn electrodes are assumed to have a radius *R*, and separated by a distance *a*. where Φ is the potential in the point *P* and r_1 and r_2 are the distances between *P* and the two middle points of the cylinders. A point *M* is defined on the yarn surface and E_O denotes the electric field strength at *M*. Both yarns, at potentials $\Phi = V_0/2$ (positive) and $\Phi = -V_0/2$ (negative) are assumed to be metallic cylindrical volumes each having the same radius *R* [142, 143] The PEDOT:PSS material is assumed to have filled in the entire space between the two cylinders. These simplifications allowed us to make a less complicated analytical calculation of the potential distribution in the selected area. For a single cylinder in an infinite space, the potential distribution in the yarn electrode is proportional to the distance from the fore mentioned point *P* and is given by $\Phi \propto \ln(r_1)$ where *r* is the distance to the center of the cylinder (yarn electrode) [144]. In case of two cylinders at opposite voltages, the potential distribution can be approximated by the superposition.

$$\boldsymbol{\Phi \propto \ln(r_1) - \ln(r_2) \quad = \quad \Phi = \mathrm{A} \ln\left(\frac{r_1}{r_2}\right)} \qquad \textbf{Equation 10}$$

The constant *A* in Equation 10 has to be determined by the boundary condition $\Phi = V_0/2$ at the left cylinder. Due to the symmetry in Equation 10, the boundary condition $\Phi = -V_0/2$ at the right cylinder is then automatically fulfilled. We then use $r_1 = R$ and $r_2 = a$ so that:

$$\boldsymbol{\frac{V_0}{2} = A \ln\left(\frac{a}{R}\right)} \quad \textbf{or} \quad \mathrm{A} = -\frac{\boldsymbol{V_0}}{\boldsymbol{2\ln\left(\frac{R}{a}\right)}} \qquad \textbf{Equation 11}$$

In the point *M* Figure 6.5, the electric field is then given by:

$$\boldsymbol{E_0} = \frac{A}{R} + \frac{A}{a} = -\frac{V_0}{2a\ln\left(\frac{R}{a}\right)}\left[\mathbf{1} + \frac{1}{\frac{R}{a}}\right] = \frac{V_0}{2a}\boldsymbol{\Psi} \qquad \textbf{Equation 12}$$

where the function *Ψ* is defined by:

$$\boldsymbol{\Psi}\left(\frac{R}{a}\right) = -\left(\mathbf{1} + \frac{1}{R/a}\right)\frac{1}{\ln(R/a)} \qquad \textbf{Equation 13}$$

A plot of the function *Ψ* is drawn in Figure 6.6. Note that for small values of *R/a* which corresponds to yarns with a small diameter, the function *Ψ* is quite steep. However, for larger values of *R/a*, e.g. *R/a > 0.2,* the function *Ψ* is almost constant.

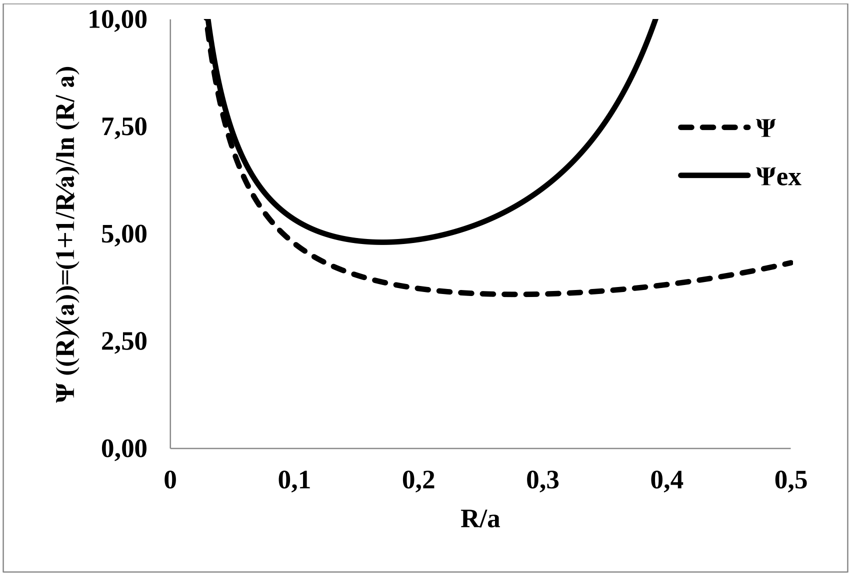


Figure 6.6 Plot of the functions $\boldsymbol{\Psi}\,(\boldsymbol{R/a}) = (\mathbf{1} + \mathbf{1}/\,\boldsymbol{R/a})/\boldsymbol{ln}\,(\boldsymbol{R/\,a})$ and the exact solution *Ψ*$_{ex.}$

Theoretically, the solution of Equation 10 is a good approximation as long as *R<<a, a* being the distance between the two yarns. An exact solution of the potential problem valid for all R/a values can be obtained by using a biaxial coordinate system [142, 145]. The exact solution is still given by the expression Equation 10 provided that both r_1 and r_2 are now the distances to the two origins of biaxial coordinate systems, which are no longer the centre points of the cylinders. The distance between the two origins is given by:

$$\boldsymbol{a}\left(\sqrt{\mathbf{1}-\mathbf{4}\frac{\boldsymbol{R}^2}{\boldsymbol{a}^2}}\right) \qquad \textbf{Equation 14}$$

Remark that $R<<a$ the expression Equation 14 equals to a, i.e. the distance between the two center points. For the electric field strength, an expression similar to Equation 10 is obtained:

$$\boldsymbol{E}_{\mathbf{0}}=\frac{\boldsymbol{V}_{\mathbf{0}}}{\mathbf{2}\boldsymbol{a}}\boldsymbol{\Psi}_{\boldsymbol{ex}}\left(\frac{\boldsymbol{R}}{\boldsymbol{a}}\right) \qquad \textbf{Equation 15}$$

Without going into all the mathematical details, we give the expression for the exact solution Ψ_{ex}:

$$\boldsymbol{\psi}_{\mathrm{ex}}=\frac{\mathbf{1}}{\ln\left(\mathbf{1}-\sqrt{\mathbf{1}-\mathbf{4}\boldsymbol{R}^2/\boldsymbol{a}^2}\right)-\ln(\boldsymbol{R}/\mathbf{2a})}\ \frac{\sqrt{\mathbf{1}+\mathbf{2}\boldsymbol{R}/\mathbf{a}}}{(\boldsymbol{R}/\mathbf{a})\sqrt{\mathbf{1}-\mathbf{2}\boldsymbol{R}/\mathbf{a}}} \qquad \textbf{Equation 16}$$

In Table 6.3 the corresponding *R/a* values are shown for the three sizes of yarn electrodes, i.e. thin, medium and thick yarns. In our experiments a is approximately 1.5 mm. The *R/a* values were evaluated from the three diameter values D_{th}, D_{tex} and D_{meas}. It is observed that the *R/a* values for the thick yarn electrode and the medium yarn electrode are in the region where the ψ function [142, 144] is almost constant (refer to Figure 6.6). This is especially true for the *R/a* values calculated from the measured diameter $D_{meas.}$

Table 6.3 The corresponding *R/a* values of the theoretical diameter D_{th}, diameter derived from Tex, D_{tex} and the measured diameter D_{meas}.

Yarn electrode	D_{th}	***R/a***	D_{tex}	***R/a***	D_{meas}	***R/a***
	μm		μm		μm	
Thin	139	**0.046**	133	**0.044**	211±48	**0.070±0.016**
Medium	208	**0.069**	201	**0.067**	312.5±43.5	**0.104±0.015**
Thick	417	**0.139**	402	**0.134**	762±61	**0.254±0.020**

The conclusion is that the ψ function according to Equation 13 which is the electric field strength at the yarn electrode surface is stronger for the thin yarn electrode compared to the medium and thick yarn electrodes. The faster the voltage decay, the less the electric energy stored in the capacitor. A stronger electric field gives rise to ions diffusing at a higher velocity and hence a faster voltage decay as shown in Figure 6.3. It must be remarked here that the agreement between theory and experiment cannot be perfect in such a case. First of all the distance a is not that accurate, because both yarns have been inserted by sewing. Secondly, the PEDOT:PSS polymer applied on the 6mm by 10mm area about the yarns, (as per the sample preparation section) does not fill in/occupy the entire area between the two yarns. A lot of space is also occupied by the non-conducting textile substrate. The PEDOT:PSS layer is also limited by the thickness of our fabric. Furthermore, the diameter of the yarn electrode itself is not constant along the yarn length due to the yarn twist and the amount of air trapped between the filaments. The variation of yarn electrode diameter is big. Lastly, it must be noted that we calculated the electric field strength at point *M* Figure 6.5. The region of high electric field is limited to the near neighbourhood of the yarn electrode.

It must be stressed that the only parameter we could find which makes a clear difference between the thin yarn electrode on the one hand and the medium and thick yarn electrode on the other hand, is the electric field strength at the electrode surface, which in turn depends on the yarn electrode diameter.

6.6 Conclusion

Three different sizes of yarn electrode of stainless steel filament yarns with different yarn diameter were used to produce three different PEDOT:PSS capacitors. The performance in terms of voltage decay of the three types of capacitors was studied and investigated. The initial perception was that the voltage decay was related to the yarn linear resistance, but this was not true. Therefore it was difficult to clarify the difference in the voltage decay graphs of the thin yarn electrode capacitor from the medium and thick yarn electrodes. From our theoretical model, yarn electrode diameter was used to calculate the electric field strength around each yarn. From this, we could state that the electric field around the yarn is stronger for a thin yarn compared to a thick yarn. This means that in our PEDOT:PSS cell concept we could not achieve a better performing device with thinner yarn of higher resistance compared to the thicker yarn of lower resistance. Overcoming of self-discharge of the device would bring better results of the capacitor.

7

Use of electric energy stored in PEDOT:PSS capacitors

The aim of this chapter was to estimate the amount of useful energy stored in the developed capacitors despite their self-discharge. Flexible capacitors were made using stainless steel yarns as yarn electrodes on textile substrate. The electrolyte material used was a dispersion of polyethylene dioxythiophene polystyrene sulphonate (PEDOT:PSS) from Ossila company. The capacitor was charged normally and used to power a calculator. This experiment was repeated up to 5 times with different devices. We opted to report the best results obtained so far with the experiments. Due to the self-discharge, it was not easy to directly determine the energy stored in the devices, therefore the energy in the cell was estimated from the energy it supplied to the voltmeter. Using the equation that relates energy to capacitance, the capacity of the developed device was estimated. Charging the developed capacitor at 1.5 V for 2 hours was good, but due to the self-discharge, the energy stored in the capacitor could barely do any work. We stretched the capacitor and charged them at an arbitrary voltage of 3 V for roughly 40 minutes. After charging the capacitor for sufficient time at 3 V, the accumulated charge in the device was about 1.2 V, but for a short time. In this experiments too, a sharp voltage drop was observed initially for a few seconds as it has been throughout the other experiments, then the voltage discharge slows down. The capacity of the developed capacitor was estimated to be 180 µF. The developed device was used to supply energy to a low power consuming calculator which was connected to it. The calculator (TOSHIBA LC-810) could run on the developed cell for 37 seconds.

7.2 Introduction

Integrating electronics into textiles and even wearable clothing has given rise to a new research area called smart textiles [103]. Electro-conducting yarns have been used for making heating garments [113], sensors [146] antennas [147] and electric interconnects [86] .Other applications can be found in the medical field [112]. A well-known example of application of conductive yarns is in textile electrodes on the clothes of a patient to monitor continuously the heartbeat. For these types of wearable textiles the power supply is an essential part of the system. Several types of capacitors or batteries that could be used in smart textiles have been investigated [47, 50, 138]. Our research is focused on a capacitor made from electro - conducting yarns (stainless steel) as the yarn electrodes and PEDOT:PSS as the electrolyte material [37, 53, 54]. It should be remarked here that it was not always clear whether one is dealing with a battery and/or a capacitor. Sometimes the word “capattery” has been used to label these devices. There was need to quantify the amount of useful energy that can be stored in the developed capacitor despite their self-discharge. The energy stored in the device after charging for two hours was calculated and converted to farads using the charge Equation 4, explained in chapter 1. The capacity of our developed devices was determined to be 180 μfarads.

7.3 Device preparation

A three layered laminate of textile substrate with the same specifications as used in our paper [53, 54] was adopted. The yarn electrodes used were pure stainless steel filament yarns from Bekintex [93] .The upper surface of the fabric was made hydrophobic using a thermoplastic polyurethane (TPU) layer from Epurex [95] except for a left out region of 10 mm by 6 mm, where PEDOT:PSS electrolyte from Ossila was applied in layers. The TPU prevented the PEDOT:PSS from spreading too much on the fabric. The PEDOT:PSS was drop coated in (7 layers) using a pipette, while the fabric was in the oven. Each layer of PEDOT:PSS was left to dry in the oven for 15 minutes at temperatures of 90-100^{0}C, before applying the next layer. Figure 7.1 shows the image of the developed capacitor.

Figure 7.1 Fabricated PEDOT:PSS capacitor with three stainless steel yarn electrodes

7.4 Charging and powering a calculator (load resistor)

By closing the switch *S*, in the charging circuit as shown in Figure 7.2, the PEDOT:PSS capacitor was charged at a constant voltage of 3 V in these set of experiments. The time dependent voltage *V(t)* across the PEDOT:PSS capacitor was recorded with a voltage metre having a high input resistance of 10 mega ohm *(MΩ)*. After a sufficient charging time (normally 2 hours), the switch *S* was opened and the PEDOT:PSS capacitor starts discharging across the voltage metre. Despite the self-discharge, a significant amount of charge is still accumulated in the cell. The energy stored in the cell was calculated as the area under the voltage decay curve. In the experiments to power the calculator, an arbitrary voltage of 3 V was used to charge the device for about 40 minutes. A load R_L (TOSHIBA LC-810 calculator) was connected in parallel to the capacitor and voltage metre as presented in Figure 7.2.

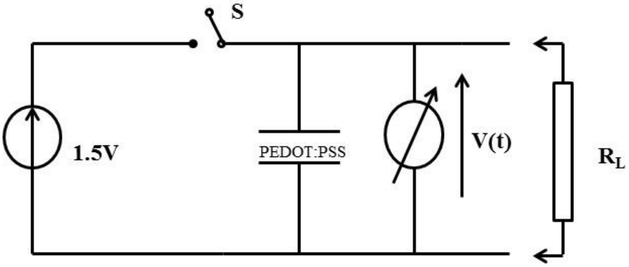


Figure 7.2 Circuit layout of Charge – discharge

Typical discharge characteristics of these developed capacitors is shown in Figure 7.3. The capacitor in these experiments were charged at different times and at higher voltage. Therefore curve *A* was obtained after charging the device for 2 hours at a constant voltage V_0 = 3 V. Curve *B* corresponds to a much shorter charging time of 40 minutes and at 3V, and curve C corresponds to charging of the capacitors for 40 minutes at 3V. The charged device is then connected to a calculator whose photovoltaic cells are well covered such that the only source of power to the calculator is from the developed devices and not from photovoltaic cells. The batteries in the calculator were also removed. The calculator connected to the capacitor was operated on for about 37 seconds, before the screen dimmed completely. This experiments were repeated up to five times, using different cells. The longest time a cell could support the calculator is 37 seconds.

For all the graphs in Figure 7.3 which represents this cells, the voltage decays very rapidly from 3 V to a value of about 1.2 V in a few seconds in the beginning,. The very beginning of this graphs is eliminated for purpose of clarity, however, the characteristics of the graph is exactly the same as with the graphs presented in the other chapters but with higher values, due to the higher voltage used. After the drastic drop of the voltage in the beginning few seconds, the voltage decay still continues but much slower. Several hours is required for a complete discharge to occur. From the results shown in Figure 7.3, it is quite obvious that the PEDOT:PSS capacitors are lossy (self-discharging). A perfect capacitor connected to a voltage metre will also show a decaying voltage due to the discharge across the input resistance of *10 MΩ*. Such a discharge curve is always an exponential function see Figure 1.12 in chapter one. But the experimentally obtained curves shown in Figure 7.3 with the PEDOT:PSS capacitors are far from exponential decay functions of a typical capacitor.

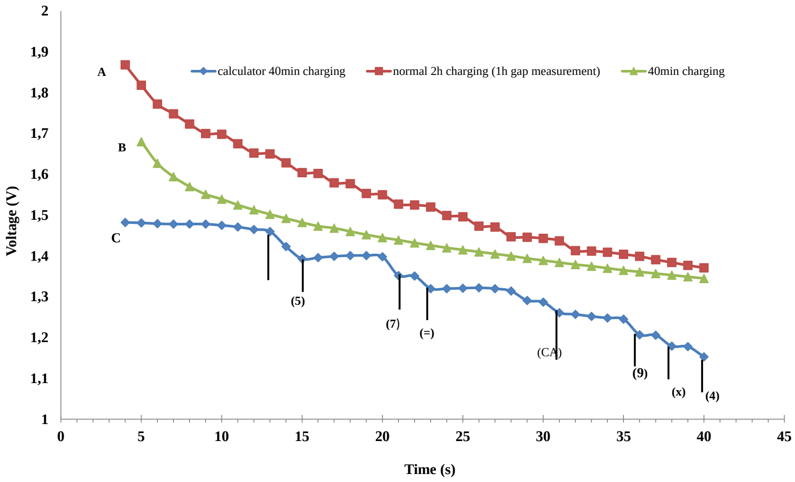


Figure 7.3 Discharge curves of PEDOT:PSS cells. ***A: 2 hours charging, B: 40 minutes charging, C: 40 minutes*** **charging and discharging with PEDOT cell connected to the calculator.**

The discharge characteristics of the developed cell is shown in Figure 7.3, all the devices are charged at 3V, but different charging time. We see that the higher the charging voltage the more the stored charge. However, in this research we did not optimize on the charging voltage.

Due to the long time constants involved in the transient characteristic graphs shown in Figure 7.3, it was not possible to use a simple capacity metre to measure the devices capacitance. Therefore we evaluated the electric energy supplied to the voltage metre as:

$$\mathbf{E_{el} = \int_{t_{ini}}^{t_\infty} \frac{v^2(t)}{R_{in}}\,dt = \int_{t_{ini}}^{t_\infty} p_{el}(t)dt} \qquad \textbf{Equation 17}$$

where $p_{el}(t) = v^2/R_{in}$ is the instantaneous electric power delivered to the voltage metre. Obviously $p_{el}(t)$ is the product of the voltage v and the current (v/R_{in}). The time t_{ini} corresponds to the time of opening of the switch S ($t_{ini} = 2$ *hours)* after the charging procedure. The integral Equation 17 has been evaluated numerically using the trapezoidal rule to approximate the definite integral. The result was found to be

$$\boldsymbol{E_{el} = 0.8101\, mJ = 0.22\, \mu W} \qquad \textbf{Equation 18}$$

The numerical quadrature was carried out from $t_{ini} = 7200s$ till $t_\infty = 19800\ s$ (*5.5* hours) because the measurement were stopped at *19800s*. The amount of energy can be attributed to an equivalent capacitance C_{eq} charged to *3V*, storing the same amount of energy as in Equation 19.

$$\boldsymbol{\frac{1}{2} C_{eq} V_0^2 = E_{el} = 0.8101\ mJ = 0.22\ \mu Wh} \qquad \textbf{Equation 19}$$

From which we get the capacitance to be:

$$\boldsymbol{C_{eq} = \frac{2E_{el}}{V_0^2} = 180\ \mu F}$$

Which is a rather high compared to electrolytic capacitors with similar dimensions.

7.5 Powering the calculator (Toshiba lc-810)

As a demonstration, a simple calculator (TOSHIBA LC-810 calculator) was powered with the textile-based PEDOT:PSS capacitor. The calculator has a liquid crystal display and is normally powered by built-in photovoltaic cells. The 4 photovoltaic cells are connected in series to provide a supply voltage around 1.6 V and their global area is about $3.6 \times 0.9 = 3.24\ cm^2$. The calculator could operate quite well with the light from an incandescent lamp of $P = 60\ W$ at a distance of 1 metre *(m)*. Taking a typical light energy efficiency of $\eta = 5\ \%$ into account and assuming the light is uniformly spread over an area of 1 m^2 we obtain the light power density on the photovoltaic cells as:

$$\boldsymbol{\frac{\eta P}{S} = 3 \frac{W}{m^2}} \qquad \textbf{Equation 20}$$

Assuming a typical efficiency of the photovoltaic cells of *10%*, we get a power delivery of *109 µW*. It must be emphasized here that this is only an estimation. Therefore, the power consumption of the calculator was also measured by connecting it to a stabilized power supply of 1.63 V. The current was then *36.84 µA* which gives us a power consumption of *60 µW.*

Obviously, during the subsequent experiments the photovoltaic cells were covered with dark paper. It was verified that the calculator was no longer useable one second after it had been covered with the dark paper. This proves that all internal capacitors can be discharged in one second.

Using the electric energy E_{el} given by Equation 18 we can estimate the time t that one PEDOT:PSS capacitor will be able to power the calculator as:

$$\boldsymbol{t = \frac{E_{el}}{P} = \frac{0.8101}{60}\frac{mJ}{\mu W} = 13}.5\ \text{s} \qquad \textbf{Equation 21}$$

In our experiment, the calculator was powered by two PEDOT:PSS capacitors connected in parallel, Although one correct cell would be able to power the calculator. Figure 7.4. shows the setup of the calculator, the voltage metre and the developed cell with two PEDOT:PSS capacitors powering a calculator (TOSHIBA LC-810), the photovoltaic cells have been covered with the blue tape. The calculator is running on the cells while being operated on.

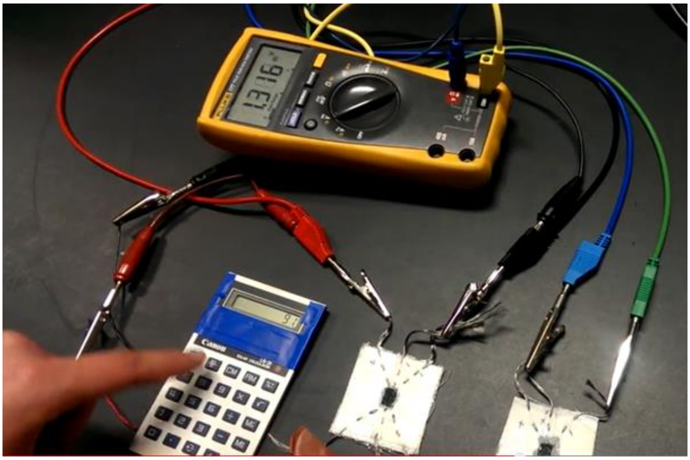


Figure 7.4 **Two PEDOT:PSS capacitors in parallel powering a calculator (TOSHIBA LC-810), the photovoltaic cells have been covered with the blue tape.**

By using two PEDOT:PSS cells and referring to Equation 21,theoretically the time of use to power the calculator is expected to be 27 seconds. Experimentally the calculator could be used for a period of 37 seconds, while operational. Two simple calculations could be performed with the PEDOT:PSS cells.

In Figure 7.3, curve *C* shows the discharge characteristic of a single PEDOT:PSS cell connected with the calculator after a 40 minutes charging at 3 V. One observes clearly that any time a button of the calculator was pressed, a sudden slight voltage drop appeared in the graph. This is due to the fact that the electronic circuits are made with CMOS technology. CMOS transistor circuits consume almost no power when the input signals do not change. Power consumption only occurs when an input signal is varying, i.e. when the calculator is performing a calculation or a number is stored in the memory, and any time a button was pressed down. The first calculation was (*5 X 7 =)*. Using the trapezoidal rule, in calculating the power of the PEDOT:PSS cells, the result was found to be 22 microwatts:

$$\boldsymbol{E_{el} = 0.8101\, mJ = 0.22\, \mu W} \qquad \textbf{Equation 18}$$

The numerical quadrature was carried out from times, ‘7’, ‘X’, ‘5’, ‘=’, CA; and ‘9’, ‘X’ ……..). A clear voltage drop is observed as shown in Figure 7.3. As soon as a constant number (‘35’ in this case) is displayed on the screen and no button are pressed, the power consumption becomes negligible and the voltage decay is mainly due to the self-discharge of the PEDOT:PSS cell.

7.6 Conclusion

A textile-based capacitor was developed from stainless steel yarn electrodes and PEDOT:PSS electrolyte. Due to the self-discharge, it was not easy to directly determine the energy stored in these devices, therefore the energy in the cell was estimated from the energy it supplied to the voltmeter. Using the equation relating energy to the capacitance, the capacity of the developed device was estimated to be 180 µF. Despite the self-discharge of the developed capacitor, two capacitors connected in parallel could power a calculator in operation for 37 seconds. Overcoming of the self-discharge of the devices would bring better results.

8

Overall conclusions and recommendations

The research presented in this work focused on developing an all textile energy storage device that is light weight, flexible, comfortable and compatible with the garment for smart textile system applications. A smart textile system is composed of sensors, actuators, data processors, interconnects, and a power supply unit. Current smart textile prototypes employ rigid, weighty batteries that come as detachable to provide power to the system; this reduces the comfort of the wearable clothing. Thus there is a need to make light weight energy storage devices which can be seamlessly integrated into textile structure as it has been done with the sensors. This should be done without compromising the comfort and other desirable aspects of the textile. The term energy storage device/cell/capacitor is used, since from the beginning, there was a mixed feeling about the developed device, and it was not clear whether it was a capacitor or a battery or a mixture.

Flexible, light weight cells, well incorporated into a textile matrix were developed.

Different types of light weight, flexible cells that are well integrated in the textile structure were made from PEDOT:PSS, conductive yarns and textile substrate. The cells have zero charge after production and they have to be charged in order to store charge. Three types of conductive yarns; stainless steel yarn, copper coated PBO yarns and silver coated PBO yarns were used differently as **yarn electrodes** in the cell development. PEDOT:PSS was used as **the electrolyte**. Cotton/polyester **textile substrate** was used as holder and the separator of the positive and negative yarn electrodes. It was discovered that out of the brands of electrolytes used, PEDOT:PSS from Ossila, was the most suitable for these charge storage devices.

Stainless steel filament yarns were the most suitable yarn electrodes for the developed cell since they accumulated more charge.

Cell development process was done mostly manually; cutting of the three square pieces of fabric, sewing in of the yarn electrodes in the upper most fabric layer, making the upper surface hydrophobic using TPU, laminating the three layers of fabric and coating of the electrolyte. Sewing of the yarn electrodes was convenient but this could be advanced to weaving in of the yarn electrodes for maintaining a perfect close separation between the yarn electrodes. The drops of the electrolyte in the drop coating process should be measured and automated, to ensure an exact amount of coating is given in all the developed devices.

Stainless steel yarn electrodes devices performed better than silver coated PBO and copper coated PBO yarn electrodes.

After charging the developed devices at 1.5 V for 2 hours, the amount of charge stored in the different types of developed cells was compared. Only silver coated PBO yarn electrode devices and stainless steel filament yarn devices could store charge. Copper coated yarn electrode devices could not store any charge. Stainless steel yarn electrodes were the best.

The amount of charge accumulated depended on the charging time to a certain extend.

The accumulated charge in the devices during discharge was proportional to the charging time. The longer the charging time, the more charge was stored in the devices until a certain limit. From these results, we decided to charge the cells for 2 hours, since this was a sufficient time. The charging voltage was not optimized. However, in most experiments we used 1.5 V.

In future work, the charging time in relation to charging voltage could be optimized.

Stainless steel yarn electrode devices could support various load resistors, and power a calculator.

The accumulated charge in stainless steel yarn electrodes cells could support high load resistors despite the self-discharge. It was possible to support load resistors of between 100-1000 kOhm. This was not possible with silver coated yarn electrode devices and copper coated yarn electrode devices. Additionally, the stainless steel yarn electrode cells could support a low power consuming calculator (Toshiba LC-810) for 37s. However, in these experiment the cell was charged at arbitrary voltage of 3V, for a shorter time of 40 minutes. The energy stored in stainless steel yarn electrode devices was evaluated and from this the capacitance was calculated, the value obtained was 180µF.

Cells made from stainless steel filament yarn electrodes were reliable and could be cycled up to 15 times.

It was discovered that the developed cells from stainless steels yarn electrodes would be charged and discharged several times (up to 15 cycles) before the cell could wear out. The residual charge was more or less in the same range for the 15 times of charge - discharge on a single cell. After the 15th cycle, onset of degradation reduced the amount of stored charge.

Dipping the cell in water or exposing the cell to higher temperatures negatively affected the charge storage.

To determine the washing effect on the developed cells, we first started by dipping in water for a few minutes before charge - discharge. We found that this had a negative effect on the accumulated charge in the devices, therefore the developed cells cannot be subjected to normal washing with water in their current state, unless some covering/packaging is used to protect them.

Charge storage was also affected negatively when the cells were exposed to temperatures between 35-40^{0}C.

Charge accumulated in the cells depended on the yarn electrode diameter.

The accumulated charge in the developed devices depended on the yarn electrode diameter, the larger the yarn electrode diameter, the more charge was stored. This could be translated to; the higher the surface area of the yarn electrode the higher the stored charge. The closer the yarn electrodes were (positive and negative), the more charge was accumulated in the cells. These experiments were conducted with stainless steel yarn electrodes.

Different types (brands) of PEDOT:PSS performed differently.

Apparently not all types of PEDOT:PSS could be used in developing the cells. Only two brands of the dispersion was good for the devices. All the printable versions of PEDOT:PSS could not work as an electrolyte. Either they were too conductive, or totally different in composition from the current PEDOT:PSS from Ossila. From the literature it is reported that the electrical properties of PEDOT:PSS depend on the ratios between the PEDOT and the PSS, and also on the conductivity enhancement agents used in the polymer mix. It would be important to investigate this polymer more, and know the exact details of it that contribute to a poor or good charge storage in the cell. Additionally, a mechanism to eliminate the self-discharge of the cell will improve on the cells efficiency.

It was a challenge to conclude on the physics/chemistry behind the charge storage devices.

There was a long debate on whether we were dealing with a capacitor or a battery, We were not quick to make this conclusion. For silver coated yarn electrode devices, we adopted the first theory from Bhattacharya *et al.*, that silver ions could migrate through PEDOT:PSS in the presence of an electric field, and be deposited as silver on the cathode when they recombined with electrons, it is further stated in literature that when metallic silver is present in a PEDOT:PSS matrix, then charge can be stored in for a long time.

However, this theory was not easy to prove with the stainless steel yarn electrodes which performed even better as charge storage devices compared to silver coated yarn electrode devices. We concluded that in the stainless steel yarn electrode cells, there is no chemical reactions per se, but a charge separation mechanism within the electrolyte when subjected to charging. This was associated with the working principle of an electrical double layer capacitor (EDLC). The charge storage mechanism in the devices with stainless steel yarn electrodes is possible due to the thin oxide layer on the stainless steel yarns. Therefore when the cell is connected to an electric field, the electrodes directly assign themselves to a negative electrode or a positive electrode based on the side connected to the power supply. The ions in the electrolyte, i.e. the PEDOT (positive) and the PSS (negative) migrate to the negative and positive electrodes respectively, hence separation of charges occurs and energy is stored in this way.

On disconnecting the charging source, the electrolyte molecules try to go back to their original position of random distribution. The PEDOT is assumed to have a positive polarity, while the PSS counterpart is of negative polarity. These molecules could also be like dipoles within the cell, during charging they are aligned in search a way that a clear charge separation occurs. When the power source is disconnected, they move back to the original position of random distribution.

The developed cells experienced self-discharge.

The developed cell could be charged for up to 2 hours, but they experienced a self-discharge (voltage decay) as soon as the charging source was disconnected. Only silver coated yarn, and stainless steel yarn electrode cells could store some charge, but not copper coated yarn electrodes. Despite this self-discharge, there was minimal level of useful accumulated charge that the cells contained for a relatively long time. The pure stainless steel yarn electrodes gave a higher minimal, useful energy of about 0.4 V for a long time whereas the silver coated yarn electrodes could give approximately 0.2 V. The copper coated yarn electrodes could barely hold any charge, hence they were not involved in further explorations.

The self-discharge of the cell is a major drawback in the developed charge storage devices, which needs to be improved to have a fully functional cell. This can be achieved by modifying the composition and the structure of the electrolyte (PEDOT:PSS) to ensure that once the charge within the electrolyte has been separated during the charging process, they don’t discharge without being connected to a load.

In conclusion, a light, flexible charge storage device, that is fully integratable into textile was developed and various aspects of it were examined. The results motivate realization of a fully functional textile-based energy storage device.

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