DESIGN AND DEVELOPMENT OF HIGH ENERGY DENSITY STORAGE SYSTEM FOR NON-CONVENTIONAL ENERGY APPLICATIONS

Thesis Submitted for the Award of the Degree of

DOCTOR OF PHILOSOPHY

in

Electronics and Communication Engineering

By

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2025

DECLARATION

I, hereby declared that the presented work in the thesis entitled "Design and Development of High Energy Density Storage System for Non-conventional Energy Applications" in fulfilment of degree of **Doctor of Philosophy (Ph. D.)** is outcome of research work carried out by me under the supervision of Dr. G. Raam Dheep, working as Assistant Professor, in the Electronics and Communication Engineering of Lovely Professional University, Punjab, India. In keeping with general practice of reporting scientific observations, due acknowledgements have been made whenever work described here has been based on findings of other investigator. This work has not been submitted in part or full to any other University or Institute for the award of any degree.

(Signature of Scholar)

Name of the scholar: Haziqul Yaquin

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CERTIFICATE

This is to certify that the work reported in the Ph. D. thesis entitled "Design and Development of High Energy Density Storage System for Non-conventional Energy Applications" submitted in fulfillment of the requirement for the award of the degree of **Doctor of Philosophy (Ph.D.)** in Electronics and Communication Engineering, is a research work carried out by Haziqul Yaquin bearing Registration No.: 11919219, and is bonafide record of his original work carried out under my supervision and that no part of thesis has been submitted for any other degree, diploma or equivalent course.

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Abstract

The increasing energy demand, decreasing fuels and limited renewable resources have forced the energy sector to search for more sustainable non-conventional energy technologies. The renewable resources have been under research and developments for the past 20 years for the same but have not been upto the mark of the consumers exponentially increasing demands. Some part of energy demand is being fulfilled by the solar thermal, solar photo-voltaic and other renewable energy resources but the limitations like time dependency, fluctuating nature, location dependency, less efficiency, high cost and space, maintenance etc. have been dominant due to which the major portion of energy demand is still under the umbrella of conventional resources adding up to the adversity of the environment and earth health as a whole. As a result, energy storage technologies are gaining interests in the field of energy research as are capable of vanishing or reducing these drawbacks of both conventional and non-conventional energy sources. The energy storage technologies can provide energy on demand, on capacity, portable, non-fluctuating, low cost, efficient, eco-friend if renewable resources utilized, etc. The major energy storage systems are solar thermal energy storage systems, electrical energy storage systems, mechanical energy storage systems, chemical energy storage systems etc., out of which electrical and thermal energy storage systems are the most potential candidates for the sustainable eco-friendly energy storage and supply technologies. The electrical energy storage systems (EES) and thermal energy storage systems (TES) as well as their collaborative hybrid systems called as multiple or hybrid energy storage systems (HES) can be boon to the energy sector and various researches are under progress.

As far as the EESSs are concerned, to supply long duration energy, batteries are there and to supply short duration energy, capacitors are there. The problem the world facing today is batteries can supply long duration energy but cannot take high power demand and on the other hand capacitors can take those high-power seeking loads but for a very short duration. This is due to the fact that energy density of capacitors is very low as compared to batteries and power density of batteries are very low as compared to their counterpart capacitors. So, there is always a big gap between the batteries and

capacitors and a single unit cannot handle both high power and long duration load demands. This gap is being filled by special electrical energy storage systems called ultra or supercapacitors. Supercapacitors have high energy density than conventional capacitors and high-power density than batteries and so are trending research interest of researchers in the field of energy storage. But still the gap between battery and capacitor have not been filled upto the mark and researches are going on. Supercapacitor is a combination of battery and capacitor and recent researches show that supercapacitors have great potential to use environmental wastes as their fundamental materials and thus fall in the category of environment friendly renewable technology. Supercapacitor technology is now most future promising for on board high power long duration emergency backup power utilizing organic wastes and reducing the use of batteries, and as a result reducing environmental impacts. The recent developments in the field of energy storage made a significant impact on in transportation, industry and domestic applications.

As far as the TES systems are concerned, the mismatch between supply and demand due to intermittent and unpredictable nature of solar radiation is a very big hurdle in the development. An optimum design of solar thermal energy storage system can reduce this drawback by supplying a constant energy to the load. Many research works are being carried out for this purpose.

This research work focuses on two energy storage systems thus firstly develops novel material based novel high energy density electrical energy storage system (EES) i.e. novel supercapacitor from carbonaceous materials like biomass wastes. The device fabricated is characterized on electrochemical work station for performance. Before making the actual device, this study looks into and compares a new type of supercapacitor to understand it better. It checks out different things like how well the supercapacitor works under different conditions. The study also sees if a computer program called MATLAB-Simulink can help make a really good model of the supercapacitor before actually making it. This research work then develops a novel material based novel solar thermal energy storage system i.e. Heat Exchanger.

The different problems addressed in this work are performance improvement for supercapacitor, novel material-method framework development for green technology based electrical energy storage system (EES), Novel material-framework development for solar thermal or simply thermal energy storage system (TES), design and development of high energy density storage systems for non-conventional energy applications, design consideration for efficient harvest of waste to energy conversion for renewable energy applications, waste management related to specific material, adding up in meeting the energy demand, anticipating the path way to solve the problem of energy insecurity, adding up to the sustainable development and reducing environmental impacts.

Experimentally, "a raw carbon waste Parali biomass is collected to develop a supercapacitor. The activated carbon developed is characterized using X-ray diffraction (XRD), Field effect scanning electron microscope (FESEM), Energy dispersive spectroscope (EDS), and Brunauer-Emmett-Teller (BET) analyses. The porous and crystalline activated carbon achieved a remarkably high carbonaceous value of 99.85% carbon from 35.71% in raw state. The specific surface area obtained is 151.42 m^2/g and the porosity (average pore diameter) is 2-10 nm of the optimized activated carbon. The activated carbon is explored as electrode material for supercapacitor in aqueous electrolyte and the specific capacitance was found to be remarkably high i.e. 247.6 F/g. The symmetrical supercapacitor device, featuring electrodes composed of carbon material, attains an impressive energy density of 54 Wh/kg along with outstanding coulombic efficiency and stability. The laboratory prototype supercapacitor has successfully powered consumer electronics, such as a DC (direct current) motor for 12.5 minutes and an LED (Light emitting diode) bulb for 14 minutes, on a single charge in each case".

On the other hand, 'Solar Thermal Energy' is used for wide range of applications such as space heating, industrial process heat, desalination, agricultural drying, and electricity generation. The present work focuses on analyzing the thermal reliability, corrosion properties, and heat transfer characteristics of shell and tube heat exchanger system for solar thermal based latent heat storage applications. In this work, Polyethylene Glycol 4000 (PEG-4000) is used as phase change material (PCM). PEG 4000 is subjected to accelerated thermal cycling tests to study the thermal reliability and corrosion properties of the PCM. The thermal reliability study of PEG 4000 shows that the change in melting temperature and latent heat of fusion after 1000 thermal cycles is -1.66 % and -1.92 %. Thermal performances such as charging and discharging

properties of latent heat storage system incorporated with PEG 4000, PCM are also analyzed in the present work for different mass flow rates of a heat transfer fluid (HTF). Further, a shell and tube heat exchanger based latent heat storage system is developed to investigate the heat storage characteristics of PEG 4000. The temperature of HTF is maintained at 80 ^{o}C and 25 ^{o}C during charging and discharging of thermal energy. The thermal charging duration for different mass flow rates of HTF at 3, 4, and 5 kg/min were 45, 65, and 85 minutes. Similarly, during discharge the mass flow rate of HTF is maintained at 2 and 3 kg/min. The thermal discharging duration for the corresponding mass flow rate is 20 and 15 minutes, respectively. The experimental results show that the PEG-4000 is stable in terms of chemical, thermal, less corrosive and has good heat transfer characteristics. Therefore, it acts as a most promising PCM for latent heat based solar thermal energy storage applications.

Hence, two novel energy storage devices viz "Parali Supercapacitor" and "PEG-400 Heat Exchanger" were fabricated and tested successfully after their respective material characterization.

Keywords— *Energy Storage, EES, TES, Biomass Waste, Chemical waste, activated carbon, Parali, PEG-4000, Supercapacitor, Electrochemical properties, Phase Change Material (PCM), Thermo-Physical Properties, Heat exchanger, Parali Supercapacitor, PEG-4000 Heat Exchanger.*

ACKNOWLEDGMENT

First of all, I would like to thank my supervisor, Dr. G. Raam Dheep for his worthy guidance, support, and suggestions, in every step of this research project during my Ph.D journey. He has an optimistic personality with helpful nature and has always made himself ready to clarify my doubts and it was a great opportunity to work under his supervision.

I would like to express my gratitude toward the entire Lovely Professional University family for providing suitable infrastructure and environment for completing my research work in a time-bound manner. Also, I like to thank the Division of Research & Development and School of Electronics and Electrical Engineering for their help and encouragement in my entire Ph.D. journey. I specially thank Dr. Gaurav Sethi, Dr. Krsihan Arora, Dr. Shanky Saxena, Dr. Prabal Gupta, Md Asif Iqbal and Dr. Yogesh Verma for their support in completing my Ph.D work. I specially thank Mr. Prashant Sir and whole team of Central Instrumentation Facility at LPU for the help and support they provided me. I thank Manoj sir and Gagan mam for their support during lab works.

I pay thank to my lovely-caring wife Ms. Aisha Ghani, my experienced-visionary fathers Dr. Abrarul Yaquin & (Late uncle) Dr. Ehtramul Yaquin and my heartful-caring mother Mrs. Yasmin Akhtar for supporting, praying, encouraging, motivating and being the back bone for me in my tough times. I pay special thanks to my brothers Mr. Zafar Imran Abdi, Dr. Imdadul Yaquin, Er. Md. Sadiqul Yaquin, Mr. Rashid Kaleem, Dr. Farrukh Shahaab, Dr. Sohail Ahmad, Mr. Ashraf Ali, my sisters Mrs. Maria Yaquin, Dr. Afreen Fayyaz, my friend Mr. Kitabuddin Ali and all my friends, relatives and teachers who supported and helped me in completing my research work. Finally and above all, I would like to thank 'The Almighty' who helped me achieve such a big milestone.

Date: 24th May, 2025 **Haziqul Yaquin**

TABLE OF CONTENTS

List of Tables

List of Figures

List of Appendices

EES : Electrical energy storage
TES : Thermal energy storage
HES : Hybrid energy storage
EESS : Electrical energy storage system
MOF : Metal-organic framework
AC : Activated carbon
CC : Current collector
PC : Parali carbon
PAC : Parali activated carbon
PACK : Parali activated carbon activated with KOH

PACH : Parali activated carbon activated with H_3PO_4
PCM : Phase change material
RDP : Relative percentage difference
EDS : Energy dispersive spectroscopy
ESR : Equivalent series resistance
PVDF : Polyvinylidene fluoride
CB : Carbon black
LED : Light emitting diode
RC : Resistance-capacitance
BET : Brunauer-Emmett-Teller
FESEM : Field emission scanning electron microscopy
EDS : Energy dispersive spectroscopy
XRD : X-ray diffraction
EWS : Electrochemical work station
CV : Cyclic voltammetry
GCD : Galvanometric charge-discharge
EIS : Electrochemical impedance spectroscopy
TGA : Thermogravimetric analysis
DSC : Differential scanning calorimetry
FTIR : Fourier transform infrared
LHF : Latent heat of fusion
PTT : Phase transition temperature
EDLC : Electrochemical double layer capacitor
HC : Hybrid capacitor
PC : Pseudo capacitor
DC : Direct current
C_p : Parallel capacitance
R_p : Parallel resistance
ckt : Circuit
R_{dis} : Self discharge resistance
R_{ct} : Charge transfer resistance
d_t : Discharging time
t_c : Charging time
t_d : Time of discharge
t_s : Time of simulation
LHS : Latent heat storage
HESS : Hybrid energy storage system
HRES : Hybrid renewable energy system
PV : Photo-voltaic
HEGSS : Hybrid energy generation and storage system
SCESS : Supercapacitor energy storage system
EV : Electric vehicle
LIB : Lithium-ion battery
PET : Polyethylene terephthalate
VPP : Vapor phase polymerization
PANi : Polyaniline
HTF : Heat transfer fluid
mΩ : Milli ohm
NMP : N-methyl-2-pyrrolidone
AB : Acetylene black

LHS : Liquid heating system

p_n : Non-activated parali carbon electrode samples (n = 1 to 5)

pk_n : KOH activated parali carbon electrode samples (n = 1 to 5)

ph_n : H_3PO_4 activated parali carbon electrode samples (n = 1 to 5)

Δm : Total mass loss or mass difference

$m(t_o)$: Initial mass at t_0

$m(t_1)$: Final mass at t_1

W/m^2 : Wattage per meter square of solar radiation

S_1 : Temperature of sensor 1 of K-type thermocouple

S_2 : Temperature of sensor 2 of K-type thermocouple

MFR : Mass flow rate

Therm-500: Thermic oil 500

DC motor: Direct current motor

PEG-4000: Polyethylene glycol-4000

Chapter 1. Introduction

1.1. Introduction to Energy Storage

The growing energy demand and dwindling resources have compelled the power sector to explore alternative energy sources. Among the most promising and inexhaustible are renewable resources such as solar, wind, and tidal energy. However, these sources are not always available and currently lack high efficiency. Ongoing research is focused on maximizing their potential by improving their efficiency.

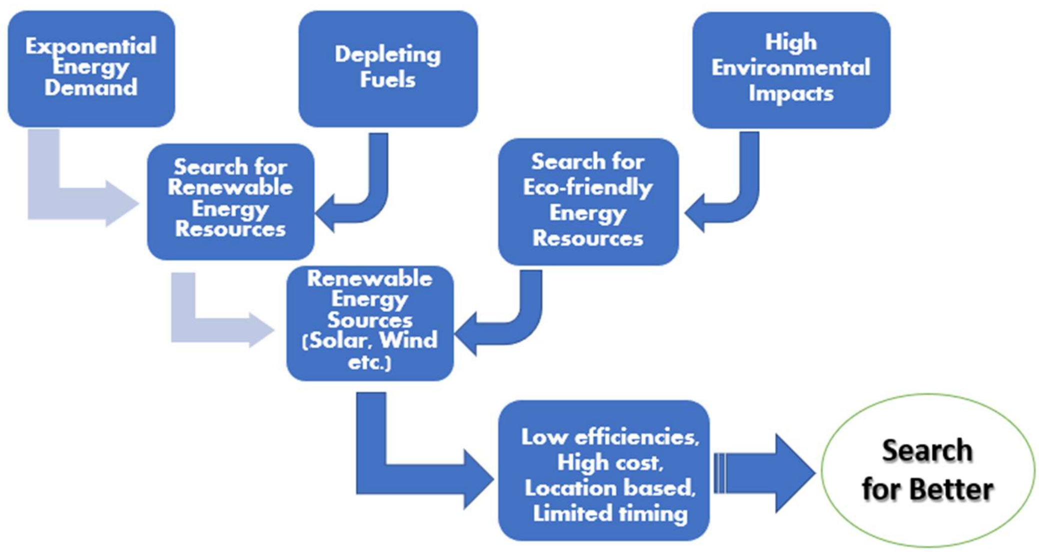


Figure 1.1: Current Scenario of Energy Technologies

Energy insecurity poses a significant challenge to our planet today, exacerbated by the rapid depletion of fossil fuels such as coal, petroleum, and natural gas. The ever-increasing global demand for comfort across various sectors of society has led to a substantial decline in these finite resources. This trend not only impacts the environment but also jeopardizes the overall health of the Earth[1]. The demand for energy and power extends far beyond basic necessities like transportation and electricity. In today's society, there is a growing desire for comfort and luxury, even at higher costs. Traditional metallic analog wristwatches have evolved into smartwatches, telephones have transformed into smartphones, and personal computers have been replaced by laptops and tablets. Additionally, there has been a shift towards energy-efficient technologies such as LED lighting, smart appliances, and electric vehicles.

From household appliances to industrial equipment and services, there is an exponential increase in the demand for high-power and high-energy solutions across various sectors, including manufacturing, healthcare, communication, banking, and military[1]. Certain devices require high-energy solutions to provide long-duration energy backup, such as laptops, mobile phones, smart-watches, and other electronic gadgets and appliances, which are conveniently powered by batteries. On the other hand, some devices require high-power solutions for shorter durations, such as electric fans, medical devices, certain household appliances, radio and telecommunication devices, and protective circuits, and these utilize capacitors instead of batteries[2]. The pursuit of comfort and luxury, in addition to meeting basic needs, has spurred researchers and scientists to devote their intellect towards fulfilling these demands as effectively as possible. The objective is to ensure that these advancements not only meet current needs but also promote sustainability for future generations, akin to the contributions of our predecessors to our own era[2].

There are numerous other instances beyond those mentioned here that demonstrate the high energy and power demands across various sectors. The challenge for our generation extends beyond merely meeting these demands; it involves doing so in a manner that ensures availability and sustainability for future generations until they develop their own resources and technologies to sustain life on Earth. This mirrors the approach taken by humanity thus far. The challenges facing our generation can be summarized as follows:

- The global depletion of fossil fuels has led to energy insecurity, posing a significant challenge worldwide. To address this issue, efforts are being made to minimize reliance on conventional sources such as coal, petroleum, and natural gas. Renewable energy sources, including solar, wind, hydro, geothermal, tidal, and biomass, offer the most promising alternatives. Given the depletion of fossil fuels, their replacement is imperative, making the transition to renewable sources a necessity.
- The use of coal, petroleum, and natural gas, along with other combustible fuels, for energy production, vehicles, and industrial activities has led to numerous environmental issues. These include global warming, greenhouse gas emissions, air pollution, water and soil contamination, ozone depletion, loss of biodiversity,

deforestation, droughts, floods, melting ice caps, rising sea levels, species extinction, adverse impacts on animal and plant health, emergence of new diseases, and disruption of the hydrosphere. Addressing these environmental challenges is paramount, and one of the most effective solutions currently available is the transition from conventional to non-conventional energy sources, particularly renewable energy sources.

- The increasing demand for high-energy, high-power devices poses a significant challenge in today's world. While some applications require long-duration energy storage, such as batteries, others necessitate high-power capabilities, like capacitors. For instance, electric vehicles rely on batteries for energy storage, but they also need high-power capabilities to support their operation. However, batteries alone may struggle to meet the power demands of heavy vehicles, while capacitors may discharge too quickly to sustain long-distance travel. Therefore, researchers are focusing on developing hybrid energy storage systems that combine the strengths of both batteries and capacitors. By leveraging renewable energy sources, such as solar and wind power, these hybrid systems aim to bridge the gap between energy storage and power delivery, ensuring global energy security and safeguarding the environment and Earth's health.

This again forced researchers to search for sustainable and stable technologies in energy demand sector. This paved way for the development of energy storage technologies like electrical energy storage (EES), thermal energy storage (TES)[74], mechanical energy storage (MES), chemical energy storage (CES), Hybrid energy storage (HES) etc. The main advantage of energy storage devices is that they are available on demand, portable, economical, simple and can supply desirable demand for desirable duration independent of time and location[1][2].

Keeping in mind the sustainable goal of reducing environmental impacts while fulfilling the energy demand, the collaboration of renewable resources, waste management and eco-friendly approach to develop the energy storage systems are in demand for the sake of the environment and sustainable development. The energy storage devices like batteries (specially Li-ion), heat exchangers, fly wheels, fuel cells, capacitors etc. are potential candidates of research in vast area and find applications in electrical, physics, chemistry, energy, electronics, power electronics, mechanical[3]. For example, Flexible Electronics make use of Flexible Capacitors and Heat Exchangers are used for Electronics Equipment Cooling etc. So both electrical and thermal energy storage systems are under main pipeline of energy storage research[4].

1.2. Electrical Energy Storage (EES) system: Supercapacitor

Although a lot of energy storage technologies are under progress, the main focus is on Electrical energy storage systems (EESS) of which the most promising candidates are Li-ion battery and capacitor. Batteries have high energy density and can supply load for long duration and capacitors have high power density but lower energy density due to which they cannot supply load for long periods of time. So as onboard sources, both capacitors and batteries mostly work in assembly[5]. This gap between the two is the major thrust of recent researches in electrical energy storage devices, also called on-demand power backups. Renewable sources are eco-friendly sources but cannot be called on emergency[6].

So recent studies have focused on developing high performance on demand energy storage devices viz batteries and capacitors from renewable resources i.e. biomass waste. A lot of researches on organic waste-based EESS have reduced the gap between battery and capacitor but to very small extent. Unanswered questions always put options to be answered and this work focuses on to minimize the battery-capacitor gap as much as possible.

The increasing demand for energy and dwindling resources have prompted the power sector to seek alternative energy sources. Renewable sources such as solar, wind, and tidal energy offer promising and sustainable solutions.

However, their intermittent availability and limited efficiency have spurred research efforts to enhance their utilization and efficiency. Consequently, researchers are now focusing on developing onboard energy storage devices to address these challenges, with lithium-ion batteries and supercapacitors emerging as the most promising candidates[7].

Lithium-ion batteries boast high energy density and are capable of supplying power for extended durations, whereas supercapacitors offer high power density but lower energy density, limiting their ability to sustain loads for prolonged periods. As a result, both supercapacitors and batteries are often used in conjunction to meet energy storage needs. Bridging the gap between these two technologies has become a key focus of recent research in the field of energy storage devices, also known as on-demand power backups[8][9].

While renewable sources are environmentally friendly, they cannot always be relied upon for emergency power needs. Hence, recent studies have emphasized the development of high-performance energy storage devices, such as batteries and supercapacitors, utilizing biomass waste as a renewable resource. Although significant progress has been made in developing organic waste-based supercapacitors and batteries, the disparity between batteries and capacitors remains relatively small. Some of the devices and machines and appliances have already started using both batteries and capacitors in combination for long duration high power demand meet like electric trucks but are not much efficient with respect to performance, cost, space and complexity.

Scientists have developed a device called supercapacitor or ultracapacitor which have high power densities and acceptable energy densities though research are going on to optimize them in terms of high power as well as energy densities as much as possible keeping environmental impacts as low as possible by anyway all can be viewed in literature reviews[10-33].

Out of the various energy storage types like flywheel energy storage, batteries, fuel cells, capacitors, thermal energy storage, hydrogen energy storage systems, the focus has majorly been shifted to bridge the gap between the capacitors and batteries to develop such devices that can provide high power than conventional capacitors for longer periods like batteries as much as possible. These devices are called supercapacitors and given in literature review chapter[34-41].

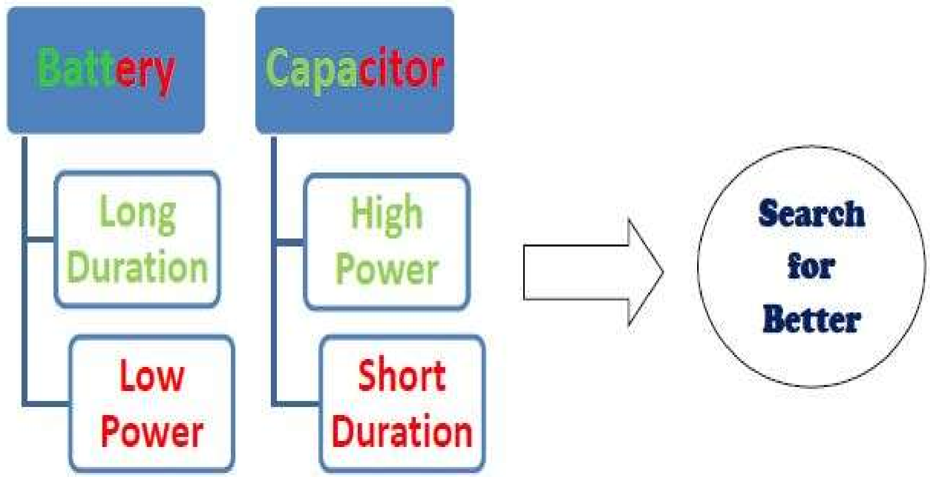


Figure 1.2: Overview of On-board, Location free, emergency, and all-time available energy technologies.

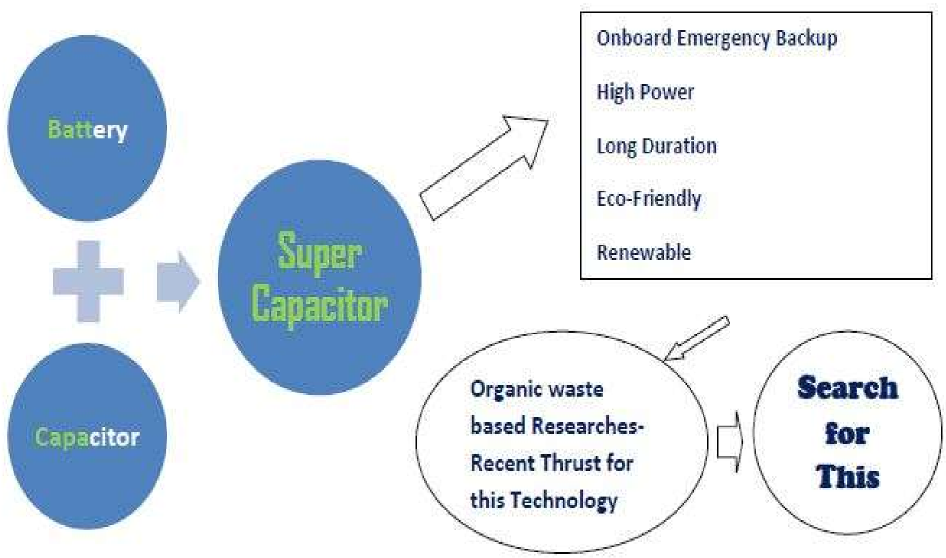


Figure 1.3: Introduction to supercapacitor technology

Supercapacitor is a better version of capacitor. A capacitor is an energy storage device. Some work on DC while some work on AC. Also, some are variable. There are various types of capacitors. Capacitors smoothen the current and voltage drop or spikes. Capacitors store electricity on their electrodes directly without any chemical reaction within, which differentiate them from batteries. A charging and a discharging battery have different chemical states, but this is not the case with the capacitor. A supercapacitor stores more energy as compared to a conventional capacitor thus provide much high power at output [17, 34]. A supercapacitor is a capacitor with much high capacitance and power density as compared to its conventional counterpart and as high energy density as possible to bridge the gap between a capacitor and battery. It is under the developmental stage and have achieved some remarkable milestone in two decades and have shown great potential in energy sector [17, 34].

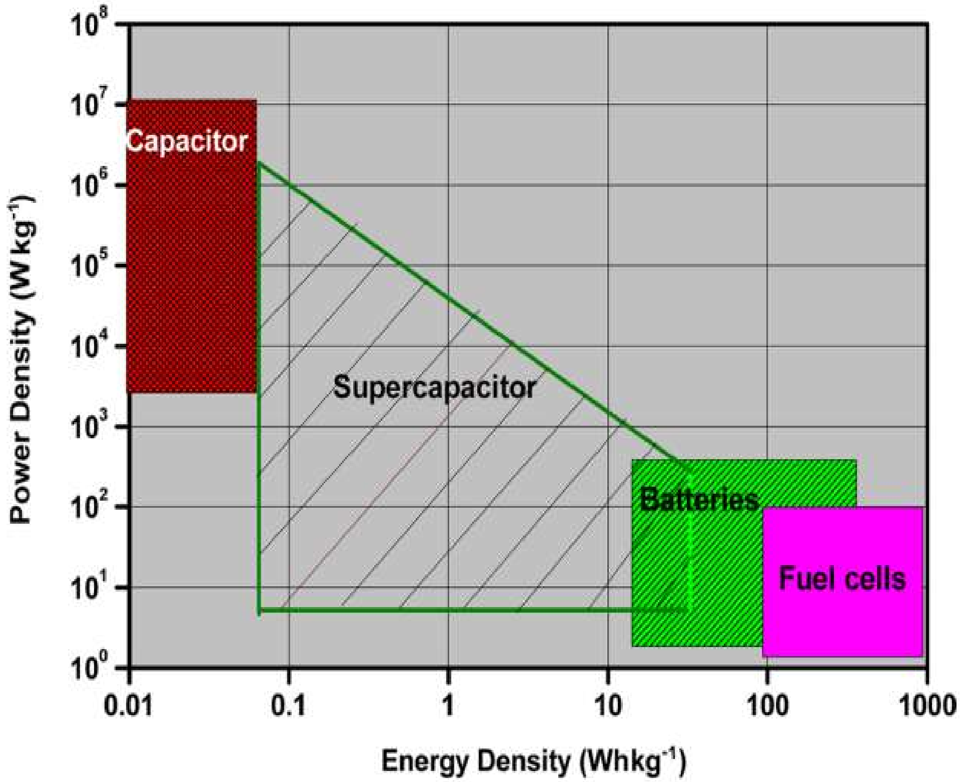


Figure 1.4: Ragone plot showing gap between batteries and capacitors [34]

Supercapacitors represent the next generation of capacitors, offering high power density compared to conventional capacitors. They comprise two electrodes separated by a thin separator, along with a binder material and an electrolyte. The performance of supercapacitors primarily depends on the characteristics of their electrodes, including type, morphology, surface area, and porosity.

Organic materials have been extensively investigated for electrode fabrication, with carbon-based electrodes garnering significant interest in recent research. To achieve high energy density and specific capacitance, electrode materials must possess a large surface area to accumulate energy and charge effectively, necessitating a porous structure with high porosity and surface area as key requirements for electrode fabrication.

Supercapacitors come in three types, offering high power but still facing challenges with low energy density compared to batteries. Improving the energy density of supercapacitors without compromising their power density is crucial for achieving on-board long-term high-power backup without relying on batteries. A good supercapacitor showcases high energy density, power density, a wide range of operating voltage, fast charging and discharging rates, minimal self-discharge, high capacitance and specific capacitance, excellent capacitance retention, long cycle lifespan, efficient charge transfer, flexibility for bending states and low temperatures, portability, wearability, low maintenance costs, safety in operation, mechanical and electrochemical stability, and consistent performance[34-38].

Challenges include mass production at low cost, hazardous exhaust, ease of disposal, material availability, and earth abundance. Low specific surface areas of carbon nano-materials, coordination breakage in metal-organic framework (MOF) based capacitors, and environmental considerations necessitate an approach that supports waste-to-supercapacitor conversion[34-38].

Parameters affecting supercapacitor performance include electro-active structural morphology, material type, conductivity, electrode surface area, porosity, pore size distribution, equivalent series resistance, electrochemical impedance, charge transfer resistance (R_{ct}), rate capability, carbon content, activation method, electrolyte composition, doping, functional groups, nitrogen, oxygen, sulfur content, and sheet resistance.

Diagnosis and improvements in supercapacitors involve in-situ and material characterization using techniques such as FT-IR, XRD, SEM-EDX, IGA-DTA, Raman spectroscopy, TEM, FE-SEM, EDAX, FT-Raman, and BET analyses[126]. Various synthesis routes, activation methods, electrode, and electrolyte materials, along with different technologies and methodologies such as pyrolysis, carbonization, activation, electrochemical deposition, etching, microwave-assisted methods, zeolite coating, thin-film electrodes, and nanotechnology, are explored[34-38].

Organic and inorganic materials, agricultural and industrial wastes, atmospheric CO_2, plastic wastes, spent Li-ion battery cathodes, waste poly(ethylene terephthalate) beverage bottles, and waste polystyrene are investigated for their electrochemical properties suitable for supercapacitors. Major electrode materials include carbon-based materials like activated carbons, carbon nanotubes, and graphene, metal oxides and hydroxides like RuO_2, IrO_2, MnO_2, NiO, Co_3O_4, SnO_2, V_2O_5, CuO, $Ni(OH)_2$, and $Co(OH)_2$, and conducting polymers like polypyrrole (PPy), polythiophene (PTh), polysaccharides, Polybenzimidazole, PEDOT, PCBM, and polyaniline (PANi). Composite materials, including carbon black-based nanocomposites, PANi@PCBM, metals, and their composites with organic materials (Metal-organic framework), PEDOT-CP composite, have recently gained interest for their improved performance [34-41].

There are three types of supercapacitors called electrochemical double layer capacitors (EDLC), hybrid capacitors (HC) and pseudo capacitors (PC). Out of the three types of supercapacitors, electrochemical double layer and pseudo capacitor are different while hybrid supercapacitor is a combination of these two [17, 34, 126].

A supercapacitor consists of two electrodes immersed in an electrolyte and separated by a thin and porous separator membrane. There are two current collectors which are conductor to connect the device to the outer power system. The whole assembly in cover and cased is shown in the figure 1.6. They consist of two electrodes separated by very thin separator, a binder material, tow current collectors connected to electrode and outer power system and an electrolyte. Ions/charge deposition and release on/from the surface of the electrode via electrochemical charge transfer processes cause their operation. Electrodes play main role in performance. A supercapacitor stores much more energy as compared to a conventional capacitor and have very long cycle life as compared to battery. It can be charged instantly and thus can absorb high spikes which is not possible with battery. It works only on DC. It has low voltage thus more numbers and space required. High self-discharging due to static or direct electricity storage is still a challenge. Using the regenerative braking technology, supercapacitors are now suitable for heavy load electric vehicles. Researchers are working on it for the integration of supercapacitors with or without batteries in small electric vehicles, though some have got remarkable results and in grid for power stability by absorbing high spikes in on-grid solar system [17, 34-38].

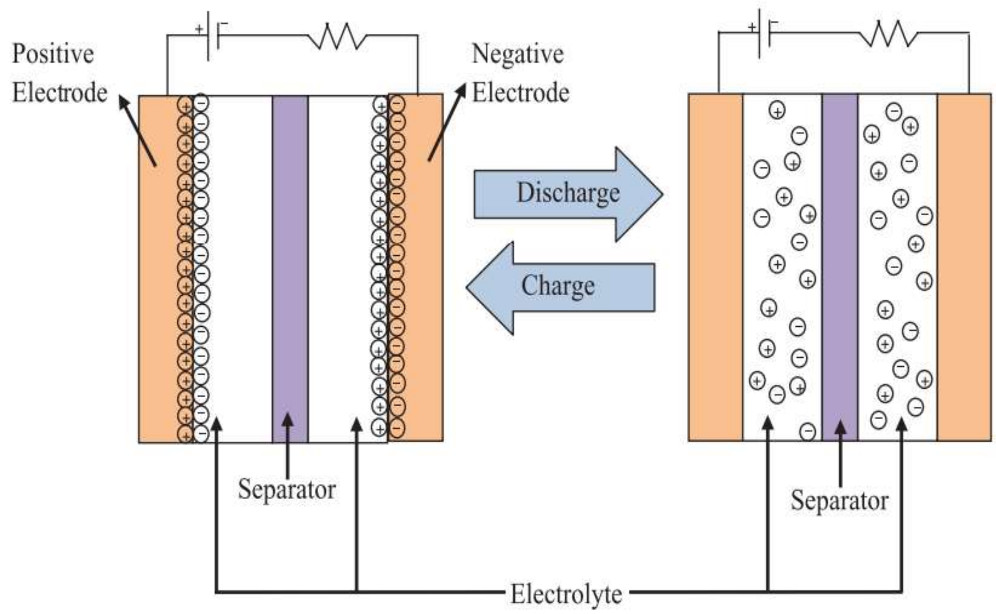


Figure 1.5: Working and configuration of supercapacitor [17]

This is electrochemical double layer supercapacitor (EDLC) and is the main type of supercapacitor and other types include pseudo capacitor and hybrid capacitor. Physical separation of charges occur at the interface of electrode and electrolyte. The positively charges cations are attracted by the negative electrode and anions are accumulated on the pores of the positive electrode during charging as shown in figure 1.5. As a result, double layers of charges are formed on both interfaces and are called electrochemical double layers so is the name of the device. Charges are stored on the surfaces of electrodes and no redox reaction occur in EDLC[17, 34-37]. Hybrid is a combination of EDLC and PC. Anyways the EDLC is the best and majorly been worked on [17, 34-37].

During discharging the energy supplied by a capacitor depends on how much voltage it has stored and that ultimately depends on charge stored and the capacitance of the device.

We know that capacitance of a capacitor is given by [17]

$$C = \varepsilon A/d \qquad \ldots\ldots\ldots..(1)$$

So, by increasing the total surface area of the electrodes on which charges have to accumulate will increase the overall effective capacitance of the capacitor which will ultimately increase the overall energy density of the device.

So as a conclusion of the theories of equations stated above, at this point one thing is clear that to have more power density and energy density, the material to be used must have low resistance, high surface area and high specific capacitance. Also, the design of the device plays vital role in the performance of the device like the distance between ions and surface of electrode [1]. In this way the promising future of energy storage i.e supercapacitor, is made and works and can be improvised to achieve the target of high energy density with keeping high power density as high as possible.

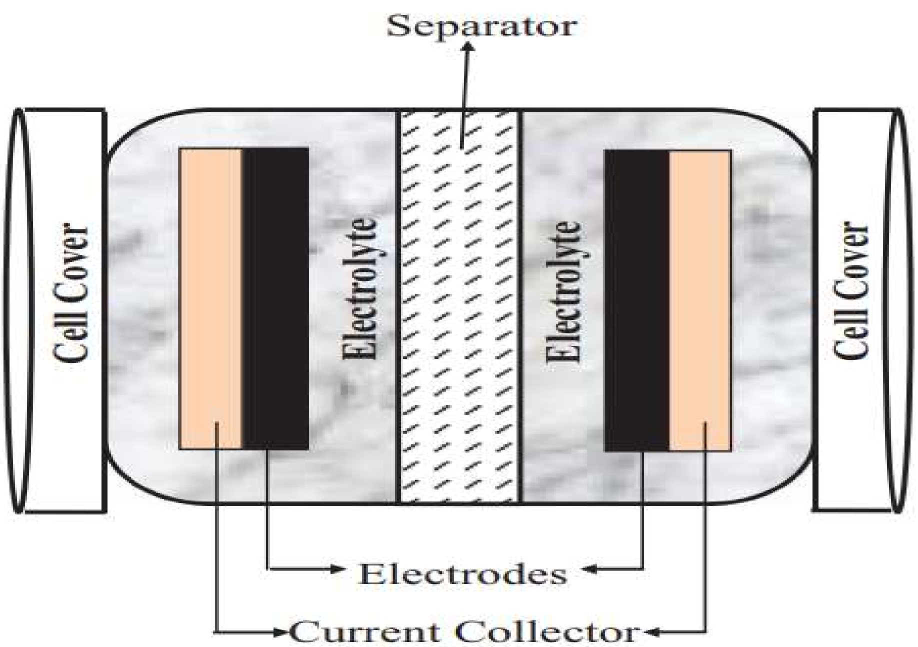


Figure 1.6: Parts of Supercapacitor [17]

Current collectors are generally metal foil or carbon filled polymers to supply current to supercapacitor. The separator and electrolyte allow ionic current between electrodes and prevents the electric current from discharging the cell and the separator also prevents the charges to directly move between electrodes. In this way the electrochemical double is developed at both the interfaces of electrodes and electrolyte and makes the capacitor charged up to almost double the value of its counterpart conventional capacitor.

Electrodes may be made up of carbons, composite materials, metal organic composite materials, conductive polymers, etc. Electrolyte can be KOH, H_2SO_4, $ZnCl_2$ etc. Current collectors are generally made of Ni-metal [17, 34].

From material synthesis to electrode and electrolyte making and from deign to configuration, there are fundamental properties that need to be at some desired range so to have the best performance from the device as a whole[40-41]. These are the parameters that need to be optimized while designing the device as they affect the performance of the device. The parameters are Specific surface area, porosity, over all resistance, overall distance between electrode surface and ions, at fabrication level and these will help in getting optimized and best performance from the device [17, 34-38].

Specific surface area: it is defined as the surface area of the material so synthesized per gram. It must be as high as possible.

Porosity: it is defined as the volume of pores and their size and morphology available after the preparation of a material for electrode of supercapacitor.

The distance between electrode surface and ions depend on the porosity and specific surface area. The overall effective impedance depends on a lot of factors like resistance of material of electrode, electrolyte, resistance of connection between electrode and current collector, resistance that come into existence during operation and these need to be optimized and reduced to get best results. The electrochemical properties include specific capacitance, energy density, power density, self-discharge, life cycle, retention capacity, charge discharge capacity, overall efficiency of the device[40]. We can only work on former list of parameters to have optimized results of final parameters which is the ultimate of goal of every research in this area.

They depend on the parameters mentioned above and must be in some range so that it can be stated that the device is good in accordance with the desired results and performance.

Specific capacitance: it is the capacitance of the cell of the device so fabricated and is given by F/g. It must be as high as possible and the range available is 20-400 F/g and more values can be a very good achievement.[54].

Energy density: it is defined as the amount of energy that the supercapacitor electrodes can store per gram of electrode. It is responsible for the longer duration of power supply and must be as high as possible. It is very low ranging from 1-10 Wh/Kg [54].

Overall efficiency is nothing but the overall performance of the device as whole which needs to be optimized as much as possible. So, all these electrochemical properties come into existence while the device is fabricated and thus depend on the parameters stated above. Good parameters at material level will give good electrochemical properties at performance level of device. Various electronics equipment powered by batteries, but small scale and flexible supercapacitors are now replacing them where high or nominal high power is needed for short or not so long time periods like flexible or small electronic gadgets and a lot more. Supercapacitor consists of two electrodes installed on two current collectors dipped in an electrolyte and separated by a very thin porous insulating membrane called separator. Ions/charge deposition and release on/from the surface of the electrode via electrochemical charge transfer processes cause their operation[17, 34-41]. The electrodes play vital role in their performance. A good supercapacitor must have high energy density and high specific capacitance[17, 34]. This depends on the material characteristics of the electrodes like type, morphology, surface area and porosity. A lot of organic materials have been explored and shown remarkable results for electrode fabrication[17, 34-38]. Carbon based electrodes are gaining interest in recent researches.

Broad area of this part of the research work is new generation power systems comprising development of high-performance supercapacitor having as high energy density along with other relevant parameters as possible without compromising power density.

Here carbon materials (Carbon, Carbon composites and Nanocomposite carbon material) are synthesized from raw carbon rich material precursor. To achieve high energy density and specific capacitance, electrode material must have large surface area to accumulate more energy and charge for which the structure must be porous[17].

So, high porosity and high surface area are major requirements of electrode fabrication. In this part of the research work, highly porous and large surface area electrode will be fabricated from organic carbon waste because carbon materials are readily available, cheap, eco-friendly, biodegradable and possess relevant properties to be used as electrode of supercapacitor. Finally, the fabricated electrode will be tested for electrochemical and other properties to have highly optimized supercapacitor. Its scope is interdisciplinary distributed from engineering, energy, material science, physics, chemistry, soft electronics, power systems, waste management, environment, industrial, agricultural, social to global level[17, 34-41].

1.3. Simulation and Optimization

Out of various devices developed throughout the world, simulation for some of them have also been performed for various internal and external variables in leu of a better visualization of their effects on the performance of the device. Simulation is nothing but modelling of a device in controlled and desirable way to optimize the desired output with respect to prefilled inputs that are the internal parameters responsible for the variation in the performance of the device. This can be done using a number software like OrCAD, PSCAD, MATLAB, etc. [42-60]. Any energy storage device have two types of parameters: the ones that are independent of outside conditions and the others that are dependent. So these parameters play a vital role in simulation of a device. A review on simulation software and modelling as well as fixed or independent parameters gives the idea of best environment to be used for this purpose of modelling, simulation and optimization. Although it is an auxiliary and hypothetical work but has been done here as objective 1 to better visualize the effects of various parameters before designing.

A supercapacitor is a capacitor with much high capacitance and power density as compared to its conventional counterpart and as high energy density as possible to bridge the gap between a capacitor and battery. It is under the developmental stage and have achieved some remarkable milestone in two decades and have shown great potential in energy sector. [17]

This part of the ongoing project focuses only on modelling and simulation of an existing model on a highly impactful platform like matlab-simulink after reviews related to the same. This section includes the forecasting of the research i.e. simulation of the device to understand the effects of various internal and external parameters on the performance of the device i.e. supercapacitor. Those parameters are Electrode material, electrolyte material, activation agent, Porosity, surface area, ESR, R_{ct}, R_{dis}, Warburg resistance Z_w, C_p, R_p, Temperature, cell voltage, terminal voltage, capacitance, charging current, discharging current and performance parameters like energy density, power density, charging time t_c, discharging time t_d, efficiency, life cycle, retention, cyclability etc. Not all but some relevant parameters have been adjusted as in previous references[42-60].

MATLAB-Simulink has been used for its simulation. Initially a pre-tested supercapacitor has been simulated here for different parameters values and the results have been tabulated for reference as a relationship with the working of the device. Some of the parameters are known from the data sheet of the capacitor in test and some are obtained by screening test and rest a few are adjusted on the MATLAB-Simulink environment to optimize the model under observation. From a number of models of supercapacitor available, the best updated model till date has been modelled here in the paper alongwith the model parameters to get best results.

The parameters available with the device are: capacitance, voltage, charging and discharging current ranges[22-41, 47].

To optimize the performance, the device must charge itself as fast as possible and discharge itself as slow as possible. Thus, maximum terminal voltage should reach soon after providing the charging current of known range and should delay in discharging when load is connected.

The value of total capacitance (C') and total terminal voltage (V) of the device are known by the data sheet of the device provided by the manufacturer. The parameters obtained after testing that can be verified mathematically are shunt capacitance value (C_p), main capacitance value (C), initial voltage (u), charging current value (I) and load value (L). The parameters that can be adjusted during simulation to optimize the results, are chosen from the range of those parameters obtained from different reference papers and are shunt capacitance (C_p), Equivalent series resistance ($ESR=R_1$), self-discharge resistance ($R_{dis}=R_2$), over-voltage protection resistance (R_3), charging (t_c) and discharging time (t_d), simulation time (t_s)[45-54].

Also point to be noted that in this modelling paper of supercapacitor, different combination of values of variables from the ranges of parameters are tried and tested to obtain the best model till date, to obtain best optimized model of the device hypothetically to get a glimpse of effects of these variables on the performance of our device and to help in the making of the device as whole.

1.4. Thermal Energy Storage (TES) system: Heat Exchanger

This part of the research act as supporting work to fulfill the goal of more than one energy storage systems. The latent heat storage (LHS) is perhaps the most ideal approach among all the thermal energy storage (TES) techniques for storing thermal energy due to its high energy density, isothermal nature, small temperature changes during charging and discharging, less space requirements and low-cost as compared to the chemical storage systems [61].

Since solar energy is a promising renewable energy resource readily available at free of cost, researchers have reported solar thermal energy storage devices for future use. The phase change materials (PCMs) are widely used in the solar thermal energy based LHS systems due to their capability of storing and releasing thermal energy during melting and solidification, respectively [64-71]. An extensive review of various types of PCMs for different types of energy storage applications was reported by Dheep and Sreekumar [64].

- **What are Phase Change Materials?**
- Phase change material (PCM) is any material that takes heat and melts and solidifies on releasing the heat[75].
- **Why choosing PEG-4000 over others?**
- The various common PCMs are Paraffin wax, Glutaric acid, Fatty acids, other chemicals, rocks, bricks etc. Out of this Polyethylene glycol (PEG-4000) is best as it has high heat capacity, high thermal conductivity, low toxicity, low cost, low viscosity and high latent heat of Fusion, which are crucial in terms of energy storage and supply back process[76].
- **How it can be useful to make thermal energy storage device?**
- The other properties like Thermal stability (LHF and PTT stability), Physical stability, chemical stability and corrosion effect on container materials need to be tested and if results are good, then PEG-4000 can be very potential in making Latent Heat Thermal Energy Storage device simply called Thermal Energy Storage (TES) device [63, 66, 72].

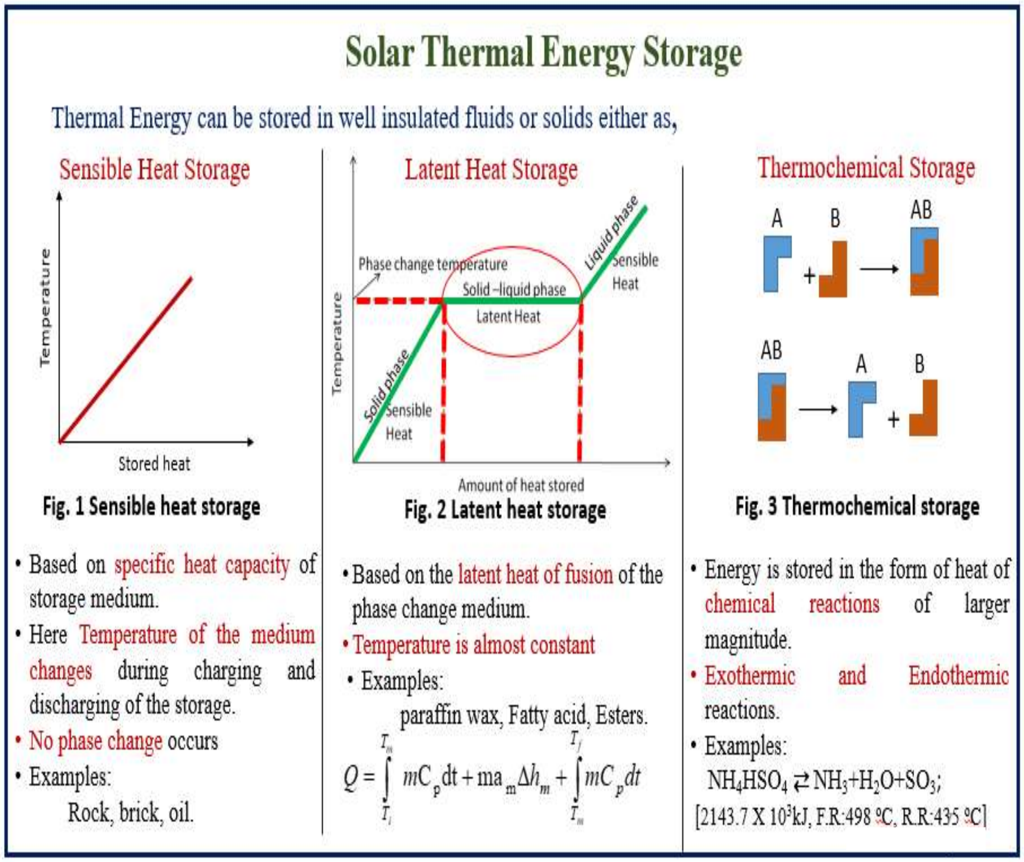


Figure 1.7: Types of solar thermal energy storage technologies

The analysis of thermal reliability of different fatty acid based PCMs such as palmitic acid, stearic acid, lauric acid, and myristic acid was reported [66]. They observed a non-consistent reduction in the latent heat of fusion (LHF) with the increase in the thermal cycle in all their fatty acid based PCMs[77].

Sharma et al. [66] reported a good thermal reliability of the commercial grade acetamide and paraffin wax at 1500 accelerated thermal cycles. It is observed a slight variation in the thermo-physical properties of the commercial grade paraffin wax above 400 thermal cycles.

Sharma et al. [72] also observed a gradual change in the thermo-physical property of the paraffin, palmitic acid, and myristic acid based organic PCMs for thermal cycling up to 1500 cycles. The amount of energy stored in a PCM depends on its phase transition temperature, latent heat capacity, and physical and chemical properties [72].

However, there are still ample opportunities to search for new PCMs for the energy storage applications.

- Solar Thermal Energy has an enormous potential to be utilized in various domestic and industrial applications (Water heating, Space heating, Drying, Industrial process heating).
- However, energy is intermittent, unpredictable, and available only during a few hours of the day.
- Therefore, it should be stored when it is available, so that it can be used during non-available hours for applications.
- Energy storage helps balance the difference between how much energy is needed and how much is available, making the system work better and saving money overall [80].

1.5. Objectives of the Research Work

The overarching objective of this research is to address the critical challenges in energy storage technologies by developing sustainable, efficient, and scalable solutions. This research focuses on leveraging innovative materials and methodologies to bridge gaps in energy and power densities, enhance sustainability, and reduce dependency on conventional resources. The four specific objectives of the research work are:

1. **To model and simulate an existing model with respect to reviews to anticipate and obtain the best possible material, method and parameter combination.**
2. **To synthesize functional carbons from potential biomasses and organic wastes with and without activation for nanomaterial based high electrical-energy-storage system.**
3. **To analyse and optimize the energy characteristics such as energy density, power density, reliability and stability and test the energy performance of newly developed novel high electrical-energy-storage (EES) system.**
4. **To study the heat transfer characteristics of different materials and to design and fabricate high thermal-energy-storage (TES) system.**

To further elaborate the above-mentioned target objectives, the following pointers will give a better picture of the objectives of the research with respect to the actual work and applications:

- **Development of a novel supercapacitor**:

- Synthesize activated carbon from agricultural waste, specifically Parali biomass, to create eco-friendly and high-performance electrodes.
- Investigate the role of activation agents (KOH and H_3PO_4) in enhancing surface area, porosity, and conductivity.
- Optimize supercapacitor design to achieve a balance between high energy density (for long-duration applications) and high-power density (for immediate energy demands).

➢ **Material characterization and property enhancement**:

- Perform comprehensive material characterization using techniques such as XRD, FESEM, BET, and EDS to evaluate structural, morphological, and chemical properties.
- Focus on enhancing specific surface area and reducing equivalent series resistance (ESR) to improve energy storage performance.

➢ **Design and development of a Thermal Energy Storage (TES) system**:

- Utilize PEG-4000 as a Phase Change Material (PCM) due to its high latent heat, thermal conductivity, and stability.
- Develop a shell-and-tube heat exchanger design optimized for thermal efficiency and durability in real-world applications.

➢ **Simulation and optimization**:

- Employ simulation tools, such as MATLAB-Simulink, to model the performance of the proposed systems under various conditions.
- Analyse the impact of material properties, operational parameters, and design configurations on device efficiency.

➢ **Integration of waste-to-energy approaches**:

- Address environmental challenges like air pollution caused by Parali burning in regions such as Punjab by converting agricultural waste into high-value energy storage materials.
- Contribute to global efforts in waste management and renewable energy adoption.

➢ **Real-world applications and impact assessment**:

- Develop systems suitable for sectors such as agriculture, renewable energy, transportation, and domestic heating.

- Assess the environmental and economic impacts of implementing the developed energy storage solutions.

This comprehensive approach aligns with global sustainability goals, offering innovative solutions to modern energy challenges while addressing environmental concerns.

1.6. Conclusion

The introduction chapter establishes the pressing need for transformative advancements in energy storage technologies. With the rapid depletion of fossil fuels and the increasing environmental degradation associated with conventional energy systems, there is a growing demand for sustainable, efficient, and environmentally friendly alternatives. By focusing on the development of novel supercapacitor and TES systems, this research provides a roadmap for achieving energy security, reducing greenhouse gas emissions, and promoting renewable energy adoption.

The chapter concludes by emphasizing the importance of integrating waste-to-energy principles with advanced material science. The use of Parali biomass and PEG-4000 not only addresses the energy demands of diverse sectors but also contributes to environmental sustainability by mitigating issues like air pollution and waste disposal. Through a combination of innovative methodologies and practical applications, this research sets the stage for significant progress in the field of energy storage.

Chapter 2. Literature Review

2.1. Problem statement of the research

Energy storage remains one of the most critical challenges in the modern energy landscape, particularly as the world transitions toward renewable energy sources. The problems can be categorized as follows:

- **Performance limitations of existing technologies**:
  - Batteries, while offering high energy density, are limited in their ability to handle high-power demands and face challenges like limited lifecycle, slow charging rates, and high costs.
  - Capacitors, on the other hand, excel in power density but are constrained by low energy storage capacity, making them unsuitable for long-duration applications.
  - The gap between these technologies creates a pressing need for hybrid solutions like supercapacitors that can bridge these limitations.
- **Environmental concerns**:
  - The widespread use of conventional batteries involves significant environmental challenges, including the extraction of rare earth materials, toxic waste generation, and difficulties in recycling.
  - In regions like Punjab, the burning of agricultural waste (Parali) contributes to severe air pollution, adversely affecting public health and the environment.
- **Thermal energy storage inefficiencies**:
  - The intermittent availability of solar energy creates a mismatch between energy supply and demand, necessitating efficient thermal energy storage systems.
  - Existing TES systems often fail to deliver consistent performance due to poor thermal conductivity, low energy density, and degradation over time.
- **Economic and scalability challenges**:

- High manufacturing costs and limited scalability of advanced energy storage devices hinder their widespread adoption, particularly in developing regions.

This research directly addresses these challenges by developing innovative supercapacitor and TES technologies, leveraging waste-to-energy principles, and employing advanced material and device design techniques.

2.2. Literatures on Modelling and Simulation

Hybrid energy storage system (HESS) comprising battery and supercapacitor was developed for remote area non-conventional energy applications using Matlab-Simulink simulation environment to stabilize the load fluctuations. The model was tested and analysed theoretically as well as numerically using Matlab-Simulink successfully[22].

A comparative study of hybrid supercapacitor and fuel cell based city bus was done using practical and Matlab-simulink based models. The simulink simulation results were up to the mark and good in accordance with the practical testing results[23]. Matlab-Simulink based real time energy management control strategy for Battery-Supercapacitor Hybrid Energy Storage System (HESS) of electric vehicle was successfully developed to supress the peak power and power fluctuations effects on baterry making use of supercapacitor[24].

A 48.6 Volt, 140 Farad supercapacitor model BMOD0140-E048, was simulated using Matlab to study the charge-discharge behaviour of voltage of the device. The computer model was derived from an electrical model and the experimental and modelling results were compared and were found to be in good agreement with each other. Also simulation helped to found that temperature rises more during charging than during discharging[25].

Design modelling, simulation and optimization of Photovoltaic-hydrogen-supercapacitor hybrid renewable energy system (HRES) for grid connected applications was done sucessfully on PSCAD/EMTDC software platform, to overcome the intermittency problems of renewable resources, peak load and load fluctuations. Battery-supercapacitor hybrid energy storage system (HESS) was modelled and integrated into a grid connected photvoltaic system with DC-DC control converter using Matlab-simulink and the simulation was done for all components separately as well as in assembly of HESS-PV system as whole. The model of the supercapacitor utilized was Maxwell BCAP3000 capacitor. The charging and discharging currents to study the capacitor on simulink were 200A and -200A respectively[26].

A novel series supercapacitor-fuel cell hybrid energy storage system as controlled power source was modelled using Matlab and compared with Simscpae PowerSystems platform sucessfully and the results were in good agreement with the experimental results[27].

A Photovoltaic-battery-supercapacitor hybrid energy generation and storage system (HEGSS) with control strategy was designed using Matlab-simulink program sucessfully to stabilize the voltage and increase the power quality of the system during peak and fluctuating demands. Advantages and disadvantages of supercapacitor was summarized and comparative performance of Lead-acid battery, Lithium ion battery and supercapacitor was also collected from various references[28].

Matlab-Simulink based passive and active design, modelling and simulation of Battery-supercapacitor Hybrid energy storage system (HESS) with control strategy for standalone Photovoltaic power system to improve the capacity and power stability of the system as a whole was sucessfully implemented. In passive system, bidirectional converter is not present[29].

Matlab-SimPowerSystems toolbox based modelling and simulation of a control converter to improve the dynamic performance of the fuel cell-supercapacitor based electric vehicle, was sucessfully done[30].

Defects in materials were detected using simulation methods accurately[42]. Important parameters determination, material characterization accuracy improvement and process development has been done using simulation[43]. Advanced material characterization for maximum recovery and utilization using simulation has been done with more accuracy for solid waste materials[44]. Lastoskie et al utilize the molecular theory[56] as well as density theory[45] to successfully characterize the porous structure of the material using simulation. This says that simulation is very useful at structural analyses.

Modelling and simulation of supercapacitor for testing its applicability for high power load was also done. Here a 12 Volt supercapacitor model was modelled, simulated and optimized usnig OrCAD lite software platform to develop the effect of varying equivalent series resistance on the charge-discharge behavior and performance of the device. The best electrical model available i.e series parallel RC model with non-linear parameters, was considered to model on the software[46]. So it is observed that not only at molecular level but at load level also the simulation technique is very useful.

Also Farcas et al did the modelling and simulation of various supercapacitors modules successfully which justifies that any model of supercapacitor can be modelled and simulated on a platform in anticipation of how the similar module will work[47]. A 14 Volt ECOND PScap350 supercapacitor model was modelled, simulated and optimized on OrCAD PSpice 9.2. The chargng was done by 10A and discharging was done by -20A of currents and the highest voltage of charging was set at 11V instead of full 14 V charging[47].

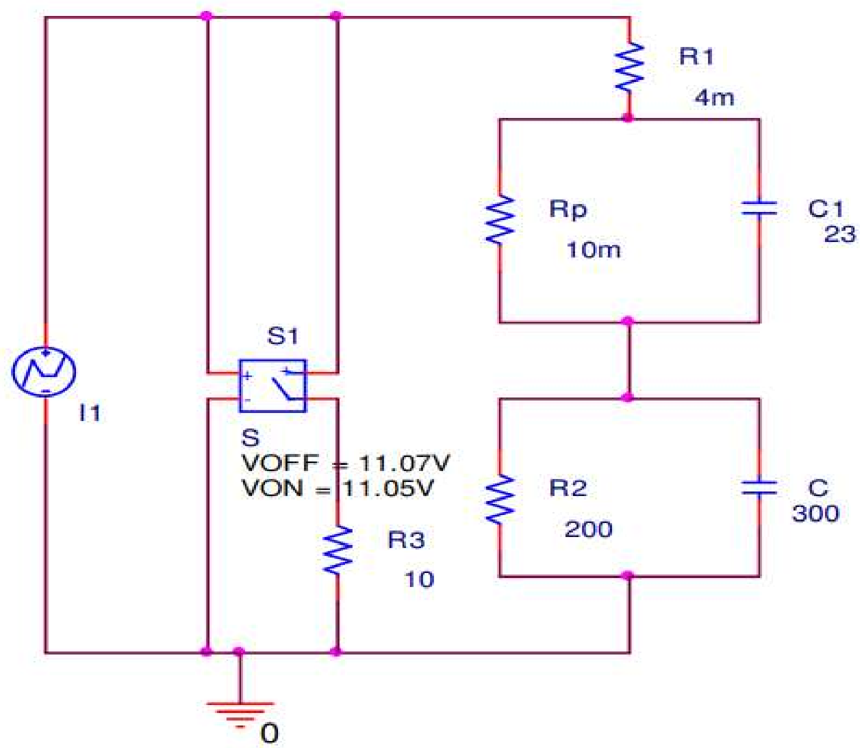


Figure 2.1: OrCAD PSpice 9.2 model of Supercapacitor derived from series parallel RC equivalent circuit with non-linear parameters of the supercapacitor[47]

Hinov et al did the great job by modelling and simulating the process of charging of an electric vehicle by a supercapacitor using the software called Matlab-simulink which proves that not only charging but discharging can also be simulated before using[48] and even before designing[47]. Designing a charging model for supercapacitor using Matlab-Simulink to be used in electric vehicles was done sucessfully[48].

A novel interior search algorithm (ISA) was developed and proposed to determine the supercapacitor parameters using Matlab-simulink from the best electrical model available. The experimental and simulation results were found to be in good agreement[49].

Development of novel solar-supercapacitor hybrid energy system as roof of electric vehicles and its simulation for various irradiance using Matlab-Simulink to reduce the battery size and weight, increase the kilometer range per hour and total power, was done sucessfully[50].

Modelling and simulation program comparison and their review was done which was very useful in terms of model and parameters and software combination decision for simulation. The comparative study on various programs and software for simulation and modelling of supercapacitor was done. The various software include Matlab-Simulink, OrCAD-PSpice, SimPowerSystems, PSCAD, Saber, Dymola and PLECS of which Matlab-Simulink was found to be best as far as supercapacitors are concerned[51].

Numerical analyses on effects of electrodes and electrolyte of supercapacitor with mesoporous electrodes were simulated and realized using mathemiatical equationes implemented on COMSOL multiphysics 5.0 software[52]. A review on comparision of various supercapacitor mathematical models available was done and one of them was realized using Matlab-simulink [53].

A comparative study on various theoritical electrical models of supercapacitors, various software to model them and their electrochemical properties with respect to batteries were done. The various software that were comparatively studied include Matlab-simulink, OrCAD PScpice, SimPowerSystems, PSCAD, Saber, Dymola and PLECS[54].

Software	Advantages	Disadvantages
Simulink	• Direct access to MATLAB • Extensive control library • Can use multiplexed signals	• Only mathematical modelling is possible • Causality problem • Simulation performance is not as good as models using only code
Sim Power System	• Electrical modelling • Less causality problems • Direct access to MATLAB and Simulink	• Complicatoins with the connection of capactor and inductors in the circuit • Require Snubbers whose values can complicate simulations • Complete behaviour of actual components is not included
OrCAD Capture	• Fast and efficient schematic editing • Has already charaterized components • Large electrical components library	• General model creation is not possible • Control elements and functions cannot be used
PSCAD	• Huge library of library electrical components • Model can be altered during simulation • Result and model both can be presented next to each other	• Only fixed step simulation can be done
Saber	• Multi domain simulation possible • Has advanced supercapacitor component • Co-Simulation with Simulink is possible	• Somewhat dated graphical interface • Saber should be running while attempting co-simulation with simulink
PLECS	• Has thermal modelling and non linear component's Library	• All effects on seminconductor cannot be studied • Electrical components can be placed only in restricted modelling area
Dymola	• Multi domain simulations with equation based modelling • Solves DAE • Parameter estimation is possible by adding model calibration	• Analyzation of results is limited • Export capabilities are also limited

Table 2.1 Comparison of various simulation softwares for supercapacitor[54]

A 2.7 Volt Maxwell Supercapacitor was modelled from its ladder equivalent cricuit and optimized using control startegy sucessfully for the effects of self discharge[55]. Characterization of various porous materials usng moleular theory and their realization by simulation was carried out sucessfully[56].

Design and simulation of supercapacitor energy storage system (SCESS) was done using Matlab-simulink sucessfully, to be implemented to STATCOMs to over come power system instability and improve real power exchange[57].

Matlab-simulink based model and simulation of supercapacitor energy storage system (SCESS) with and without STATCOM, to draw comparision between the two, to over come power system instability and improve real power exchange capacity, was done. The results were better for the supercapacitor hybrid STATCOM system than that of STATCOM alone[58].

Molecular dynamics were utilized to model and simulate and study the graphene supercapacitors sucessfully[59]. Also Drammonda et al worked at low order mathematical modelling of supercapacitor using spectral methdos[60].

2.3. Literatures on Electrical energy storage: Supercapacitors

Reviews on materials specially carbonaceous materials for the electrodes of supercapacitor were documented by different studies, e.g. carbon-composite materials[10], carbon nanotubes and activated carbon[11], Graphene carbons[12] and nano-carbon and metal oxide based composite materials[13]. A complete useful introduction about supercapacitor as discussed in introduction chapter was given by Sinha et al[14].

Activated carbons from various biomass sources were studied by Gan Y. X. which suggested that activated carbons can be obtained from a biomass which is a source of carbon[15].

Biomass based materials can be very potential candidate for supercapacitor electrodes was suggested by Wang et al[16].

Review on electrode fabrication based on different carbon materials was given by Manaf et al[17].

Also a review on status and current researches on characterization and biomass derived carbon materials for supercapacitors was presented[18]. In their review, Shanmuga P. M. et al. examined the use of carbonaceous materials, both activated and non-activated, as electrode materials in supercapacitors. They analysed the materials using various characterization techniques (FT-IR, XRD, Raman, FESEM, TEM) and evaluated their electrochemical performance through GCD and CV measurements[18].

Complete review on materials and methods for supercapacitor electrodes was documented[19].

Characterization techniques were documented for supercapacitor for power electronics applications by Zubieta et al[20].

A comparative study of Li-ion battery, supercapacitor and other devices for automotive applications in a very useful manner was documented by Pasquier et al[21].

A Photovoltaic-battery-supercapacitor hybrid energy geenration and storage system (HEGSS) with control strategy was designed using Matlab-simulink program sucessfully to stabilize the voltage and increase the power quality of the system during peak and fluctuating demands. Advantages and disadvantages of supercapacitor was summarized and comparative performance of Lead-acid battery, Lithium ion battery and supercapacitor was also collected from various references[28]. These results are very useful while designing the real time device.

Advantages of Supercapacitor	Drawbacks of Supercapacitor
High power density	Low energy density
Quick charging/discharging	Very high self-discharge rate (≈1–2 days)
Does not blow up in case of accidental direct short connection	Series connections are needed to obtain higher voltage and need a balancing circuit
Stops accepting energy when it becomes fully charged	Terminal voltage and state of charge is directly proportional
Internal ESR is extremely small (≈0.01 Ω)	Price and market delivery depends on not used widely
Extended lifetime and long shelf life (4–5 year)	Supplies power for a very short duration
Environmentally safe and no gas emissions	Highest dielectric absorption

Table 2.2 Advantages and disadvantages of supercapcitor[28]

Parameters	Lead-acid Battery	Lithium-ion Battery	Supercapacitor
Specific energy density (Wh/kg)	10–100	150–200	1–10
Specific power density (W/kg)	<1000	<2000	<10000
Cycle life (cycles)	1000	5000	>500000
Charge discharge efficiency	70–85%	99%	85–98%
Fast charge time	1–5 hour	0.5–3 hour	0.3–30 sec
Discharge time	0.3–3 hour	0.3–3 hour	0.3–30 sec
Calendar life (year)	5–15	10–20	20
Cost	100 $/kWh	400 $/kWh	2500 $/kWh

Table 2.3 Comparative table of performance parameters of LI battery, Lead acid battery and supercapacitor[28]

Argyrou et al discussed and simulated the hybrid system comprising battery-supercapacitor for Photo-Voltaic (PV) applications[31]. On the other hand Karangia et al demonstrated a hybrid system having battery-supercapacitor for use in Electric Vehicle (EV)[32].

Carbon materials for high voltage supercapacitors were discussed by Liu et al[33].

Lokhande P. E. et al. provided a comprehensive review of supercapacitors, including different methods for electrode and electrolyte synthesis, the electrochemical properties of these materials, and the key factors influencing supercapacitor performance. Their review also highlighted the dominance of lithium-ion batteries and supercapacitors in renewable energy storage and backup power applications[34].

Li C. et al. investigated the latest developments in supercapacitors that utilize carbon nanostructures as electrodes. Activated carbon electrodes have consistently delivered exceptional performance in these devices. Notably, researchers have been exploring methods to convert atmospheric CO_2 into usable carbon materials. This review by Li C. et al. delves into the chemical aspects of such conversions, along with the potential challenges and future possibilities [35].

Shen Y. reviewed the impact of hydrothermal carbonization on hydrochar derived from biomass and plastic waste. The review focuses on how this process affects the hydrochar's chemical structure, including crosslinked polymers, surface porosity, functional groups, elemental composition, and ultimately, its reactivity and fuel properties. The potential applications of carbon materials derived from hydrochar were also explored [36].

Vangri M., Pryor T., Jiang L. et al. provided a comprehensive overview of supercapacitor types, recent advancements in materials and fabrication methods, and their potential impact on future supercapacitor technology. They also discussed the challenges that need to be addressed [37].

Kausar A. reviewed the current state and emerging trends in polybenzimidazole-based nanocomposites for supercapacitors, gas separation, and reinforced materials, including fuel cells. The review also explored how the architecture of these nanocomposites influences their performance [38].

Selvaraj T., Perumal V. et al. focused on recent advancements in supercapacitors, particularly those utilizing biomaterials like polysaccharides for energy storage. Their review covered the latest developments in charge storage mechanisms, electrode and electrolyte materials, with an emphasis on bio-derived materials [39].

Selva M. explored the role of nanotechnology in designing high-performance nanomaterials and devices from biowaste feedstocks. The review highlighted recent advancements in environmental and energy applications derived from both animal and plant biomass [40].

Su F. et al. examined the current state of graphene-based supercapacitors, their future potential, and the remaining challenges. Graphene, a two-dimensional material, has shown remarkable promise in supercapacitors. To address some limitations of pure graphene, researchers have developed graphene derivatives using nanotechnology. However, large-scale, cost-effective production techniques remain a hurdle that needs to be overcome [41]. A comparative study on various theoritical electrical models of supercapacitors, various software to model them and their electrochemical properties with respect to batteries were done. The various software that were comparatively studied include Matlab-simulink, OrCAD PScpice, SimPowerSystems, PSCAD, Saber, Dymola and PLECS[54].

Parameters	Batteries	Electrolytic capacitors	Carbon EDLC
Specific Capacitance (F/g)	N/A	N/A	20-100
Specific Power or Power Density (W/Kg)	<1000	>10000	500-1000
Specific Energy or Energy Density (Wh/Kg)	20-150	<0.1	1-10
Operating Voltage (v)	Low	High	<3
Working Temperature (^{0}C)	-20 to 60	-55 to 125	-40 to 70
Charge-Discharge Cycles	~1500	>>10^6	>10^6
Efficiency	0.7-0.85	~1.0	0.85-0.99

Table 2.4: Comparative parameters of different types of capacitors with respect to batteries[54]

Su X. et al. examined a recent advancement in supercapacitor research: studying electrode materials in real-time (in-situ mode) to improve performance [84]. Xu B. et al. reviewed the latest developments in supercapacitors based on metal-organic frameworks (MOFs). They also discussed the future challenges and potential of these materials. [85]. Duraisamy E. and Prasath A. et al. developed and analysed activated carbon derived from spent honeycomb biomass. They used various techniques (XRD, FT-IR, Raman spectroscopy, SEM, HR-TEM, and BET analyses) to characterize the material. This activated carbon was then employed as an anode in half and full Li-ion battery cells, as well as an electrode in aqueous and non-aqueous electrolyte supercapacitors. The team used cyclic voltammetry and galvanostatic charge-discharge studies to evaluate both prototypes, finding that the supercapacitor exhibited good energy densities in various electrolytes. [86]. Sun Y. and Xue J. et al. created a symmetrical supercapacitor with a nitrogen-doped porous carbon derived from quinoa. This carbon material boasted a high surface area, good specific capacitance, and excellent rate capability. The supercapacitor was successfully tested with both aqueous and organic electrolytes, achieving a promising energy density of 9.5 Wh/kg in the aqueous electrolyte. [87].

Zou Z. and Jiang C. developed hierarchical porous carbon with a large amount of medium-sized pores (mesoporosity). This carbon, derived from leftover rice using a potassium hydroxide activation method, displayed a high specific surface area, high specific capacitance, high specific energy density, and good capacitance retention. The energy density reached 22.6 Wh/kg at a power density of 21.5 W/g. Additionally, the capacitance retention remained impressive at 87% after a current density of 1 A/g, and the specific capacitance was 153.2 F/g at 0.2 A/g[88]. Wu X. and Lei G. et al. synthesized functionalized hierarchical porous carbons from bean dregs using a simple hydrothermal process followed by potassium hydroxide activation. By adjusting the activating agent to carbon material ratio, they obtained a material rich in N/O functional groups, resulting in high specific capacitance and decent rate performance. The team also fabricated a symmetrical supercapacitor using an aqueous electrolyte that delivered good results. The energy density reached 9 Wh/kg with 6 M KOH and 25.9 Wh/g with 1M Na_2SO_4.[89]. Ji Y. and Deng Y. et al. prepared low-cost multi-heteroatom doped porous carbons derived from soybean dregs. They then anchored ultrathin cobalt oxide nanosheets onto the carbon surface to create a composite material. This composite exhibited high energy density, high charge transfer efficiency, high specific surface area, and low electrochemical impedance. Both aqueous and solid-state supercapacitors were fabricated and tested, demonstrating a good combination of power and energy density, along with excellent retention capacity[90]. Wang Y. and Liu R. et al. reported a novel approach for synthesizing heteroatoms doped hierarchical porous carbons derived from chitin using potassium permanganate ($KMnO_4$) as the activating agent. They fabricated an electrode and a flexible solid-state symmetrical supercapacitor from this material. The resulting electrode displayed a large surface area, a well-developed hierarchical porous structure, and numerous N/O functional groups. The supercapacitor exhibited ultra-high specific capacitance, good rate characteristics, remarkable electrochemical stability, high energy density, and excellent stability in a KOH solution electrolyte. [91]. Mehare M. D. et al. synthesized hierarchical porous carbon from onion peel using a double crucible method. This method yielded a low-cost supercapacitor with high specific capacitance and excellent capacitance retention. Additionally, they fabricated a symmetrical supercapacitor device that achieved high energy density, remarkable electrochemical stability, and exceptional capacitance retention. [92]. Lu W. and Cao X. et al. prepared high surface area, high specific capacitance, and excellent capacitance retention activated carbon from pitaya peel using KOH as the activating agent. The prepared material demonstrated promising specific surface area and specific capacitance. [93]. Li Z. and Chen D. et al. developed a zinc ion hybrid supercapacitor based on porous carbon derived from biowaste (pencil shavings) and zinc foil. This supercapacitor achieved high energy density and outstanding cycling stability (capacity retention). Furthermore, when they integrated the optimized carbon cathode into quasi-solid-state hybrid supercapacitors with a unique anti [94]. Yana J. and Shena J. combined carbonization and etching to create N, S, and O-doped activated carbon from helianthus pallets using KOH activation. This unique material had a template-like microarchitecture and high doping content. Electrodes made from it displayed good specific capacitance, and the resulting asymmetric supercapacitor exhibited long life, good rate capability, and excellent capacitance retention. [95]. Lee K. and Shabnam L. produced carbon aerogel electrodes from jackfruit and durian. The high nitrogen doping in durian aerogel was preserved during synthesis. The researchers compared the specific surface areas and mesopore proportions of both aerogels. Electrochemical characterization using CV, GCD, and EIS revealed high specific capacitance, excellent cycling stability, and good charge performance for both durian and jackfruit aerogels in a two-electrode configuration[96]. Yu F. and Ye Z. developed 3D mesopore-dominant hierarchical carbons from plane tree bark using a one-step pyrolysis-activation process with nano ZnO as a mild activator. This material exhibited an ultra-high mesopore area and low oxygen content. The resulting electrode showed high capacitance and a wide capacitive potential range in both aqueous and organic electrolytes. It achieved a high cell voltage and high specific capacitance in organic electrolytes. Interestingly, a mismatch was found between the specific capacitance and traditional methods for measuring specific surface area[97]. Pratheepa I. M. and Lawrence M. synthesized a novel material: CuZnCdO metal nanoparticles with varying concentrations. They used fresh A. heterophyllus leaf extract as a reducing agent and graphene oxide derived from dead A. heterophyllus leaves. The structural properties of the reduced graphene oxide (rGo)/CuZnCdO composite were analysed using various techniques. The material displayed the highest capacitance and good stability. The device fabricated from this material exhibited high energy and power densities, as visualized using a Ragone plot[98]. Natarajan S. and Kaipannan S. employed hydrothermal treatment to create supercapacitor electrode material from the sandwich-layered $Li_{0.32}Al_{0.68}MnO_2(OH)_2$ of spent lithium-ion battery (LIB) cathodes. This regenerated material demonstrated high specific capacitance in a half-cell configuration. Furthermore, the researchers fabricated an asymmetric supercapacitor by pairing the regenerated material with orange peel-derived nanoporous carbon (activated with 3.5KOH). The composite material device exhibited excellent specific capacitance, long cycle life, good capacitance retention, high energy density, and high-power density at a working cell voltage of 1.8 V. This asymmetric device outperformed its symmetric counterpart [99]. Wen Y. and Kierzek K. produced porous carbon nanosheets from waste polyethylene terephthalate (PET) beverage bottles. They achieved this through the combined effect of catalytic carbonization and KOH activation. The material exhibited an ultra-high specific surface area, a hierarchical porous architecture, and a large pore volume. The device made from this material displayed high specific capacitances in various electrolytes (6M KOH, 1M Na_2SO_4, etc.), good energy density, and high capacitance retention [100]. Ma C. and Min J. proposed a method for creating 3D hierarchical porous carbon from waste polystyrene. Their method involved carbonization and KOH activation using Fe_2O_3 as both a catalyst and template. The resulting material showcased high specific capacitance and excellent rate performance in a three-electrode device. The fabricated symmetrical capacitor exhibited high energy density in an aqueous electrolyte[101]. Li M. et al. developed a composite material named MnO_2@R for asymmetric supercapacitors. This composite comprised porous carbon derived from rambutan peel and MnO_2. They reported a specific capacitance of 137 F/g at 0.5 A/g. The asymmetric supercapacitor displayed high electrochemical performance with a power density of 1283.7 W/kg, energy density of 9.2 Wh/kg, and 82% capacitance retention after 5000 cycles. This research suggests that rambutan peel and similar biomass materials are promising for developing supercapacitor electrode composites [102]. Ates M. and Kuzgun O. created two types of microscopic compounds (binary and ternary nanocomposites) containing conductive carbon black (CB) and manganese dioxide (MnO_2), potentially for use in supercapacitors. They used a range of techniques to analyse the structure of these materials (FTIR, RAMAN, etc.) and then studied how well they store electrical energy (electrochemical properties) in symmetrical supercapacitors (devices with identical electrodes). The ternary material (with a 1:1:3 ratio of components) exhibited the best ability to store electrical charge (highest specific capacitance) in sulfuric acid solution (1 M H_2SO_4) at a slow scan rate (1 mV/s). The supercapacitor made with this material achieved impressive energy storage and delivery rates (high energy and power densities). Additionally, a scientific model (equivalent circuit model) was used to understand the electrical behaviour of the device. Interestingly, the ternary material in a 1:1:5 ratio displayed exceptional longevity (excellent long cycle life) and maintained its charge storage ability well (good capacitance retention) [103]. Li B. and Beltran L. H. et al. fabricated a solid-state, flexible supercapacitor using a novel material. This composite material combined a conductive polymer (PEDOT) that was polymerized in a vapor phase (vapor phase polymerized) with a cellulose paper matrix (PEDOT/CP). This unique material functioned as both the electrodes and the current collector in the device. The supercapacitor exhibited low electrical resistance (low sheet resistance) and strong adhesion (survived scotch type test). It also demonstrated remarkable stability (excellent stability). The device's ability to store electrical charge (specific capacitance) was among the highest ever reported. This exceptional performance is attributed to the vapor-phase polymerization process (VPP) and the porous, fibrous structure of the cellulose paper matrix. The supercapacitor can withstand being bent (high bending conditions) and is considered environmentally friendly (easily disposed) because it doesn't release harmful fumes (significant hazardous exhaust)[104]. Chen R. et al. developed a flexible hybrid supercapacitor using a combination of one-dimensional nanowires and two-dimensional nanosheets. These nanosheets were arranged in a specific, mesh-like structure (2D mesh like vertical structures) composed of nickel cobalt sulfide ($NiCo_2S_4$) and nickel hydroxide ($Ni(OH)_2$). The supercapacitor displayed a high ability to store electrical charge per unit area (high aerial capacity), excellent capacity retention (84.7%), and good performance at varying charge/discharge rates (excellent rate performance). It also exhibited remarkable stability over many charge/discharge cycles (high cycling stability) and a high energy density. The research team suggests that nickel cobalt sulfide and nickel hydroxide are promising materials for use in portable, wearable, and flexible nano-electronic devices[105]. Devese S. et al. designed a new supercapacitor with minimal self-discharge (lowest self discharging) and exceptional stability (excellent stability). This device was constructed using readily available materials (earth abundant material) and employed potassium chloride (KCl) as the electrolyte solution. Notably, this design did not significantly compromise other performance aspects. Supercapacitors typically lose some charge over time (self-discharge). To address this issue, the researchers introduced a zeolite coating on the electrodes. This coating significantly improved the device's ability to retain its charge (charge retention) compared to electrodes without the coating (enhanced by 350%). They measured the specific capacitance, coulombic efficiency (a measure of charge conservation), and charge retention of the supercapacitor [106]. Chen X. and Mi H. et al. produced a hierarchical porous carbon microfiber (CPZ-AC) containing nitrogen atoms (N-doped) using a unique approach. This approach involved growing a hybrid precursor material (polyaniline (PANi) and ZIF-8) on cotton thread and then applying a chemical activation process. The resulting material exhibited exceptional properties for use in supercapacitors (ideal capacitive properties). The solid-state supercapacitor fabricated with this material (CPZ-AC//PVA/KOH(gel)//CPZ-AC) achieved the best combination of power delivery and energy storage capacity (highest power and energy density combination) along with satisfactory stability over charge/discharge cycles (decent cycling stability)[107]. Ramadan A. et al. investigated incorporating a fullerene derivative called PCBM (Phenyl-C60-Butyric acid Methyl ester) into a conductive polymer known as PANi. They achieved this using a chemical process involving oxidation and polymerization. The resulting nanocomposite material, a blend on a microscopic scale, was then employed to fabricate a supercapacitor electrode. This electrode was subsequently evaluated in an electrolyte solution containing potassium hydroxide at a concentration of 2M. Amongst various PANI@PCBM combinations (where x represents the amount of PCBM added, with values of 0, 2.5, 5, and 10), the PANI@PCBM5 electrode exhibited the most impressive performance. It displayed a specific capacitance of 2201 Farads per gram, which is double that of a pure PANi electrode. Additionally, it delivered an energy density of 61.9 Watt-hours per kilogram, a power density of 2250 Watts per kilogram, and maintained a remarkable 96% capacity retention (indicating high stability) even after 1000 charge-discharge cycles.

Furthermore, it demonstrated a rate capability of 73% at a high current density of 10 Amps per gram [108]. Biomass based electrodes have low such results comparatively. The various calculation equations have been taken from[126]. Various waste biomasses and other materials have been utilized and converted to useful carbon materials like waste coffee grounds[109], polysaccharides carboxymethyl cellulose and citric acid[110], oxygen content reduced biomass based activated carbon[111], electrochemical properties of biomass derived activated carbon[112], coconut kernel for supercapacitor[113], coconut kernel for LI-battery[114], ultrathin mesoporous graphitic carbon[115], bagasse waste[116], sunflower seed shell[117], argan (Argania spinosa) with KOH activation[118], nitrogen doped porous carbon from biomass waste[119], rotten carrot[120], graphene aerogel[121], sisal[122], mixed/composite biomass waste[123], Palm Spathe[124], CO_2 activated coal and coconut shell[125], spent honeycomb[126], advanced materials[127], cassava peel waste[128], willow catkins[129], waste coffee beans[130], general biomass[131], leftover rice[132], bean dregs[133], bamboo[134], silkworm cocoon[135], pumpkin[136] and composite biomass[137].

2.4. Literatures on Thermal Energy Storage: Heat Exchanger

Solar energy is intermittent and cannot be predictable, therefore it is necessary to develop an energy storage system for such renewable energy sources[62].

Solar thermal or simply thermal energy storage (TES) system using latent heat and sensible heat tends to be most suitable energy efficient technology for solar thermal applications such as drying, industrial process heat and space heating applications.

Among the TES techniques, the latent heat storage (LHS) system is the most ideal approach of storing solar thermal energy due to high energy density, isothermal nature, small temperature difference during charging and discharging, less space requirements and low cost compared to chemical storage systems[63]. PCMs are the materials which has the capability to store and release thermal energy during melting and solidification. The amount of energy stored in PCM depend on the sensible and latent heat storage properties of the material. PCMs have pulled in expansive consideration in the field of the thermal management systems and solar thermal energy applications[65]. The extensive review of the various PCM, recent development in the latent heat storage system and different geometries of shell and tube systems is presented by Raam Dheep et al[73]. The properties such as thermal reliability, thermo-physical property, chemical stability and encapsulation of PCMs was also explained to develop the latent heat thermal energy storage system. Ahmet Sari et al[72] reported the thermal reliability studies on fatty acids such as palmitic acid, stearic acid, lauric acid, and myristic acid. The study reveals that the reduction in latent heat of fusion (LHF) for all PCM was not consistent with an increase in the thermal cycle. Atul Sharma et al[66] presented 1500 accelerated thermal cycling on commercial grade PCM such as stearic acid, paraffin wax, and acetamide. The result indicates that the acetamide and paraffin wax were practically good in thermal reliability during the cycling. Stearic acid melts at an extensive range of temperature and also shows huge variation in LHF. Different geometries of a latent heat storage system reported by G. Jegadheeswaran et al. [78], to improve the LHS, among them shell and tube systems were more frequently used. Vyshak et al[79] hypothetically revealed a near investigation of the complete melting time of PCMs stuffed in three compartments of various geometric arrangements: cylindrical, rectangular, and shell-and-tube. Thermal reliability studies on pure paraffin wax and paraffin wax carried out on 400 cycles were reported by Saw Chun Lin et al.[67]. The paraffin wax is suitable for solar heating application after thermal cycling there is a slight variation in their thermo-physical properties observed. Thermal and chemical reliability test on paraffin, palmitic acid, and myristic acid for thermal cycling up to 1500 cycle shows a gradual change in the thermo-physical property of the organic PCM was reported. The scope of this part of the work is to investigate the thermal reliability in latent heat of fusion and phase transition temperature, thermal and chemical stability of PEG-4000 for thousand thermal charging and discharging cycles. This study focuses on the compatibility of PEG-4000 for stainless steel, copper, and aluminum as container materials for medium temperature storage application. The thermal behavior in the vertical shell-and-tube thermal energy storage unit is examined. The thermal behavior and heat transfer characteristics of the shell-and-tube system during charging and discharging processes are examined. The impact of significant parameters in the performance of vertical shell-and-tube heat storage unit is investigated during this study. These properties will help developing an efficient thermal storage system for thermal comfort in building applications [81].

2.5. Research Gap

After review of literatures on Modelling-Simulation, Material-Methods for electrical as well as thermal energy storage systems, following conclusions are drafted:

Environment Friendly Green Technologies are need of the hour in energy sector. Energy storage systems are future of energy storage sectors. Simulation on Matlab-Simulink environment of a virtual device can be done before fabricating the actual device to draw outline of the work pathway to be followed. High energy density 'Electrical energy storage' (EES) system without compromising their high-power density called 'supercapacitors' are one of the potential candidates in the field of electrical energy storage. The device can be fabricated from electrodes made up of carbonaceous materials specially 'activated carbons'. High specific surface area will yield ultimately to energy density. 'Thermal energy storage' (TES) systems called 'heat exchangers' or 'space heaters' are potential candidates in the field of thermal energy storage. They can be fabricated utilizing waste materials which have good thermal and physical properties. High thermal and physical stability will ultimately yield to high energy density in the device [82].

As a conclusion of the literature review, following research gaps have been identified on the basis of whom the objectives have been formulated:

- MATLAB environment is best to model and simulate an energy storage device, but some models like ESSP48 not yet simulated in it.
- High specific surface area Activated carbons never prepared from Parali, i.e. "Parali Activated Carbon"
- Parali Activated Carbons never used to develop novel Electrical Energy Storage Systems (EES), e.g. "Parali Supercapacitor"
- PEG-4000 Phase change material never used to develop Thermal Energy Storage Systems (TES), i.e. "PEG-4000 Heat Exchanger"

2.6. Objectives of the proposed work

1. **To model and simulate an existing model with respect to reviews to anticipate and obtain the best possible material, method and parameter combination.**
2. **To synthesize functional carbons from potential biomasses and organic wastes with and without activation for nanomaterial based high electrical-energy-storage system.**

3. **To analyse and optimize the energy characteristics such as energy density, power density, reliability and stability and test the energy performance of newly developed novel high electrical-energy-storage (EES) system.**
4. **To study the heat transfer characteristics of different materials and to design and fabricate high thermal-energy-storage (TES) system.**

The four objectives of energy storage systems viz. simulation, functional material synthesis, electrical energy storage and thermal energy storage device fabrications and their performance studies and optimization. All together help achieve the goal of high energy density storage system for non-conventional energy applications.

Here the concept of simulation is utilized for optimizing the electrical energy storage system/device to be fabricated. After simulation, the fabrication of 'Electrical Energy Storage (EES) device which is a two stage process i.e. 'synthesizing optimized functional carbon' for electrodes of the device and then 'fabricating and analysing the Electrical Energy Storage (EES) device'. In this way the first objective of simulation helps synchronize and anticipate the potential device possibilities. So **objective 1** focuses on **"Modelling and Simulation".**

Then the objective 2 is followed to prepare the optimized functional material for the device to be fabricated. Now since making the material as well as the device is a vast and time-consuming rigorous research work, so the **objective 2** is only limited to **"Functional material synthesis, analyses and optimization".**

As a next step of the research work, the electrical energy storage (EES) device is fabricated and studied. So is covered in **objective 3** as "**Fabrication and analyses of electrical energy storage (EES) device called Supercapacitor".**

In objective 4, other potential material is explored to develop a parallel energy storage system with some other technology called as 'Thermal Energy Storage (TES)' system. This is done, keeping in mind, the scope of futuristic 'Hybrid Energy Storage (HES) system'. Since the material characterization, optimization as well as thermal energy storage device called "Heat exchanger" fabrication could have done seamlessly in one go, so all work from material characterization to device fabrication (TES) was done in **objective 4** as a last stage of the complete proposed research work broadly including the **"Fabrication and analyses of thermal energy storage (TES) device called Heat Exchanger".**

The main goal of the project is design different (i.e. two) energy storage systems/devices. The discussions and documentation including all other parts and stages of the research work as mentioned above, will thus broadly be done in two main/broad headings i.e. **Electrical energy storage (EES) and Thermal energy storage (TES) systems/devices.**

2.7. Conclusion of Literature Review

The literature review highlights the significant progress made in the development of energy storage systems while identifying critical gaps that this research aims to address. Supercapacitors have emerged as promising candidates for bridging the gap between batteries and capacitors, yet their energy density remains a limiting factor. Similarly, TES systems show potential for renewable energy integration but lack the thermal reliability and scalability required for practical applications.

This research builds upon these advancements by:

- Utilizing agricultural waste like Parali to synthesize activated carbon electrodes for supercapacitors, enhancing energy density and sustainability.
- Developing a TES system using PEG-4000, demonstrating superior thermal performance and long-term reliability.
- Combining experimental insights with simulation-based optimization to achieve innovative and scalable solutions.

By addressing these gaps, the research aims to contribute significantly to the fields of sustainable energy storage and waste management.

Chapter 3. Methodology

3.1. Introduction to Methodology

This research adopts an integrative and multi-disciplinary approach, encompassing experimental design, material characterization, device fabrication, performance evaluation, and simulation-based optimization. The methodology ensures a systematic and scientific exploration of novel energy storage systems to meet modern energy demands. The key aspects of this approach are detailed as follows:

3.1.1 Experimental Design:

The experimental design involves precise planning and execution of procedures to develop and test the proposed supercapacitor and Thermal Energy Storage (TES) systems. This includes:

- **Material Selection:** Parali biomass is chosen as the raw material for activated carbon due to its abundance, high carbon content, and environmental relevance in addressing stubble-burning issues. PEG-4000 is selected for its high latent heat, thermal stability, and cost-effectiveness as a Phase Change Material (PCM).
- **Chemical Activation:** Chemical agents such as KOH and H_3PO_4 are utilized to activate the Parali biomass, enhancing its porosity and surface area, which are critical for energy storage applications.
- **Device Design Considerations:** Detailed engineering considerations for electrode and heat exchanger design ensure optimal energy and thermal storage performance.

3.1.2 Material Characterization:

Material characterization is pivotal to understanding the physical, chemical, and electrochemical properties of the synthesized materials. Advanced techniques include:

- **X-ray Diffraction (XRD):** Used to determine the crystalline structure and phase composition of the activated carbon.
- **Field Emission Scanning Electron Microscopy (FESEM):** Provides high-resolution images to analyse surface morphology and pore structure.
- **Brunauer-Emmett-Teller (BET) Analysis:** Measures specific surface area and pore size distribution to evaluate the suitability of the material for supercapacitor applications.

- **Energy Dispersive Spectroscopy (EDS):** Used to determine elemental composition, ensuring high carbon purity and minimal impurities in the activated material.

For PEG-4000, tests such as Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are conducted to evaluate phase transition behavior, thermal reliability, and decomposition characteristics over multiple cycles.

3.1.3 Device Fabrication:

The fabrication process focuses on creating functional prototypes for both supercapacitor and TES systems.

- **Supercapacitor Fabrication:** The activated carbon is mixed with binders such as Polyvinylidene Fluoride (PVDF) and conductive additives to form electrodes. These electrodes are assembled with a separator and an electrolyte in a coin-cell configuration, ensuring a compact and efficient design.
- **TES Fabrication:** A shell-and-tube heat exchanger is developed, incorporating PEG-4000 as the PCM. The design ensures efficient heat transfer and minimal thermal losses, with materials chosen for their corrosion resistance and durability.

3.1.4 Performance Evaluation:

Comprehensive testing is conducted to validate the performance of the fabricated systems.

- **Electrochemical Testing for Supercapacitors:**
  - Cyclic Voltammetry (CV): Assesses the charge-discharge behaviour and specific capacitance at various scan rates.
  - Galvanostatic Charge-Discharge (GCD): Evaluates energy density, power density, and long-term cycle stability.
  - Electrochemical Impedance Spectroscopy (EIS): Measures resistance parameters such as equivalent series resistance (ESR) and charge transfer resistance.
- **Thermal Testing for TES Systems:**
  - Latent Heat and Phase Transition Analysis: Ensures consistent heat storage and release over multiple cycles.

- Corrosion Studies: Investigate the chemical compatibility of PEG-4000 with container materials such as stainless steel and aluminium.
- Flow Rate Optimization: Determines the effect of heat transfer fluid (HTF) flow rates on charging and discharging times.

3.1.5 Simulation and Optimization:

Simulation plays a critical role in predicting and optimizing device performance before large-scale implementation.

➢ **MATLAB-Simulink Modelling:**

- Simulates the behaviour of supercapacitors under various operating conditions, including variations in current, voltage, and resistance.
- Analyses the impact of electrode properties, electrolyte composition, and activation methods on device efficiency.
- For TES systems, simulation evaluates heat transfer dynamics and PCM behaviour under real-world scenarios.

➢ **Design Parameter Optimization:** Simulation results are used to refine design parameters, such as electrode thickness, electrolyte concentration, and heat exchanger geometry, ensuring peak performance.

➢ **Scalability and Sustainability Considerations:** The methodology emphasizes scalability and sustainability, ensuring that the developed systems can be implemented across diverse applications and industries.

Environmental Impact Assessment: The use of Parali biomass and PEG-4000 aligns with global sustainability goals by addressing agricultural waste management and promoting renewable energy integration.

Cost Analysis: Efforts are made to minimize production costs while maximizing efficiency, making the systems accessible for widespread adoption.

Sector-Specific Applications: The methodology tailors the energy storage solutions to meet the needs of sectors such as agriculture, renewable energy, and domestic heating, enhancing their practical relevance.

This comprehensive methodology integrates experimental rigor, material science, engineering principles, and simulation-based insights, ensuring the reliability, efficiency, and scalability of the proposed energy storage systems. By addressing both performance and sustainability, this approach sets the foundation for transformative advancements in the field of energy storage.

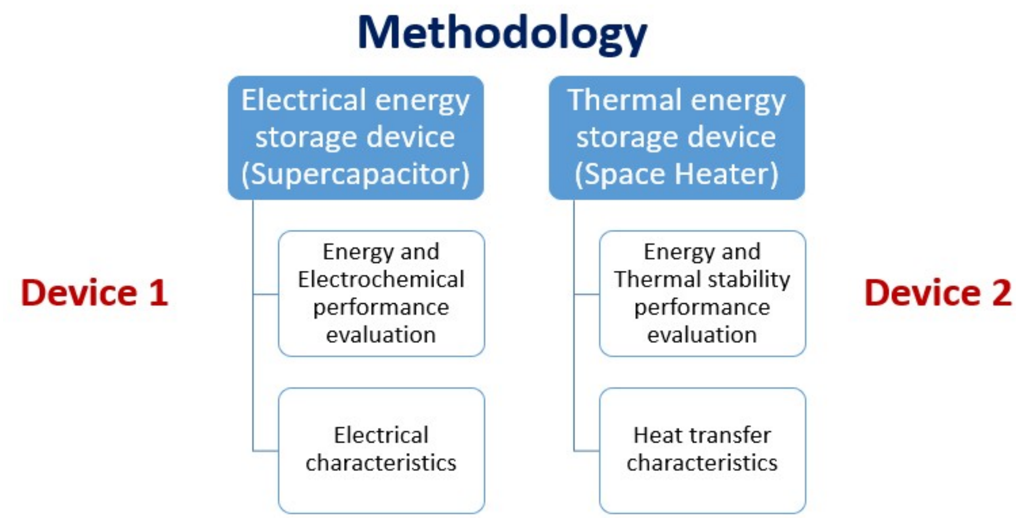


Figure 3.1: Full methodology of research work

3.2. Electrical energy storage (EES): Parali Supercapacitor (Device 1)

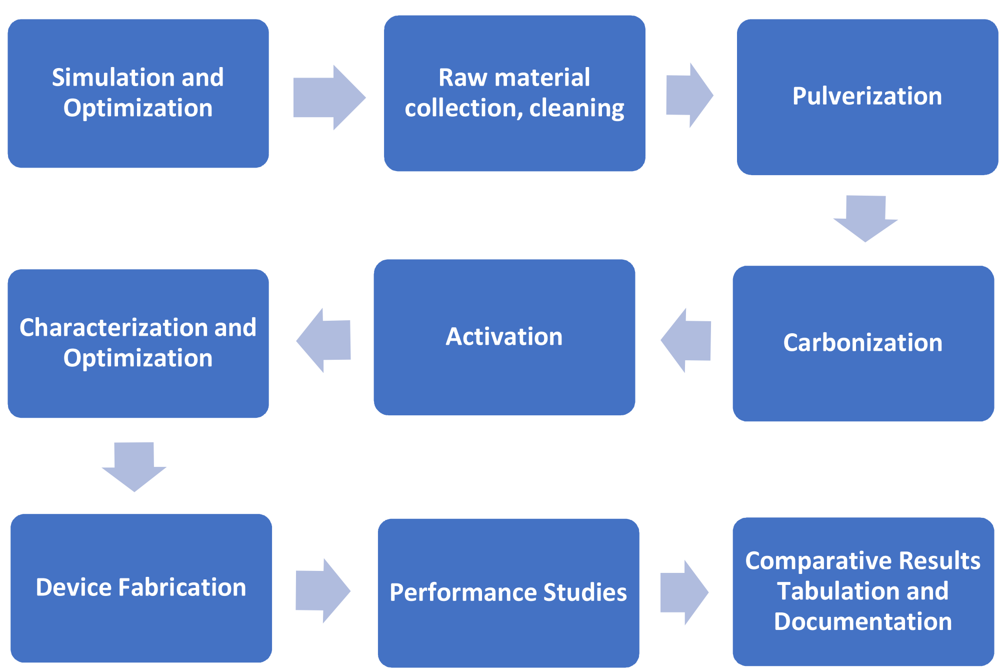


Figure 3.2: Methodology to design electrical energy storage (EES) system

Before any hardbound material and device fabrication, simulation are very useful technique to anticipate the potential of the device to be made. Simulation also helps to understand things better before proceeding any research work especially when it is going to be lengthy and hectic. For this purpose only a rigorous review of literatures and then the simulation of a model with various possible variations of different parameters was done. Various software as well as models are available for such simulations.

The research work is focused on design and development of high energy density storage systems for non-conventional energy applications. Modeling and simulation will be done before fabricating the real time device to understand the effects of various internal and external parameters on the performance of the device i.e. supercapacitor on Matlab-Simulink environment. Those parameters are Electrode material, electrolyte material, activation agent, Porosity, surface area, ESR (Equivalent series resistance), R_{ct} (Charge transfer resistance), R_{dis} (self-discharge resistance), C_p (Non-linear or shunt capacitance), R_p (non-linear or shunt resistance), Temperature, effective capacitance, charging current and discharging current as well as performance parameters like energy density, power density, charging time t_c, discharging time t_d, efficiency, life cycle, and retention. Not all but some relevant parameters have been optimized using Matlab. MATLAB-Simulink environment has been used for its simulation. The key to a powerful supercapacitor lies in its electrodes. Ideally, these electrodes should be able to store a lot of energy (high energy density) and hold a large electrical charge (high specific capacitance). This ability is heavily influenced by the makeup of the electrodes themselves, including the type of material used, its overall form (morphology), how much surface area it has, and whether it's riddled with tiny pores (porosity). Recently, researchers have been buzzing about the potential of organic materials for crafting these electrodes. Carbon-based options, in particular, are attracting a lot of attention. To maximize both energy density and specific capacitance, the material needs a vast surface area to effectively store more energy and charge. This is where porosity comes into play – a highly porous structure with a large surface area is crucial for top-notch electrode design

As far as the actual work is concerned, in this section of the research work, for the fabrication of optimized material and “Electrical energy storage” device from it, high carbon source will be used to generate functional carbon for supercapacitor electrodes. The raw biomass will be turned down to high carbonaceous material by pre-carbonization and then subjected to activation using an acid (activation agent) and then characterized using various spectroscopies like "XRD (X-ray diffraction), FESEM (field effect scanning electron microscopy), EDS (energy dispersive spectroscopy) and Brunauer-Teller-Emmett (BET) analyses". The results shown great potential as a candidate for supercapacitor. The various electrochemical studies on electrochemical work station (EWS) will be performed including CV (Cyclic voltammetry) and GCD (Galvanometric charge-discharge) analyses.

The modelling and simulation of a model of supercapacitor is done following the procedures of optimization done in [47], while the fabrication of supercapacitor device is done according to the work done and calculation equations given in [126].

3.3. Thermal Energy Storage (TES): PCM Heat Exchanger (Device 2)

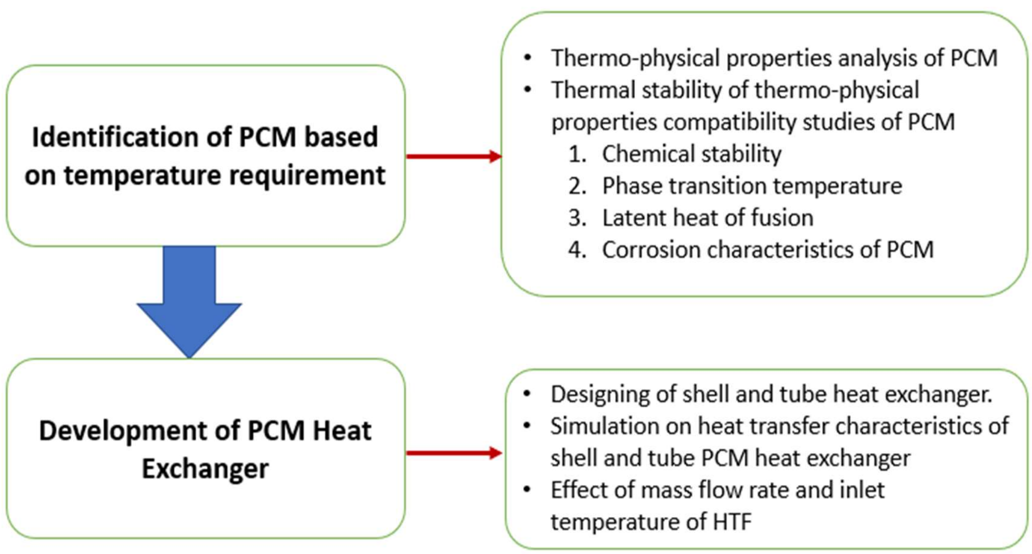


Figure 3.3: Basic scheme of the thermal energy storage system

For the development of the thermal energy storage (TES) system called space heater or simply heat exchanger, the material identification and characterization and optimization will be done so that can be better utilized for the device fabrication.

As an initial step after identification of a perfect and unused phase change material, the thermal and physical properties analyses of that material will be done on the basis of which the further processes will be done.

In this section of the research work, investigation of the properties of a waste chemical or any suitable material will be identified and then analyzed for its thermal as well physical properties for its suitability as an organic non-paraffin phase change material (PCM) in the design and development of “shell and tube based solar thermal latent heat energy storage” applications.

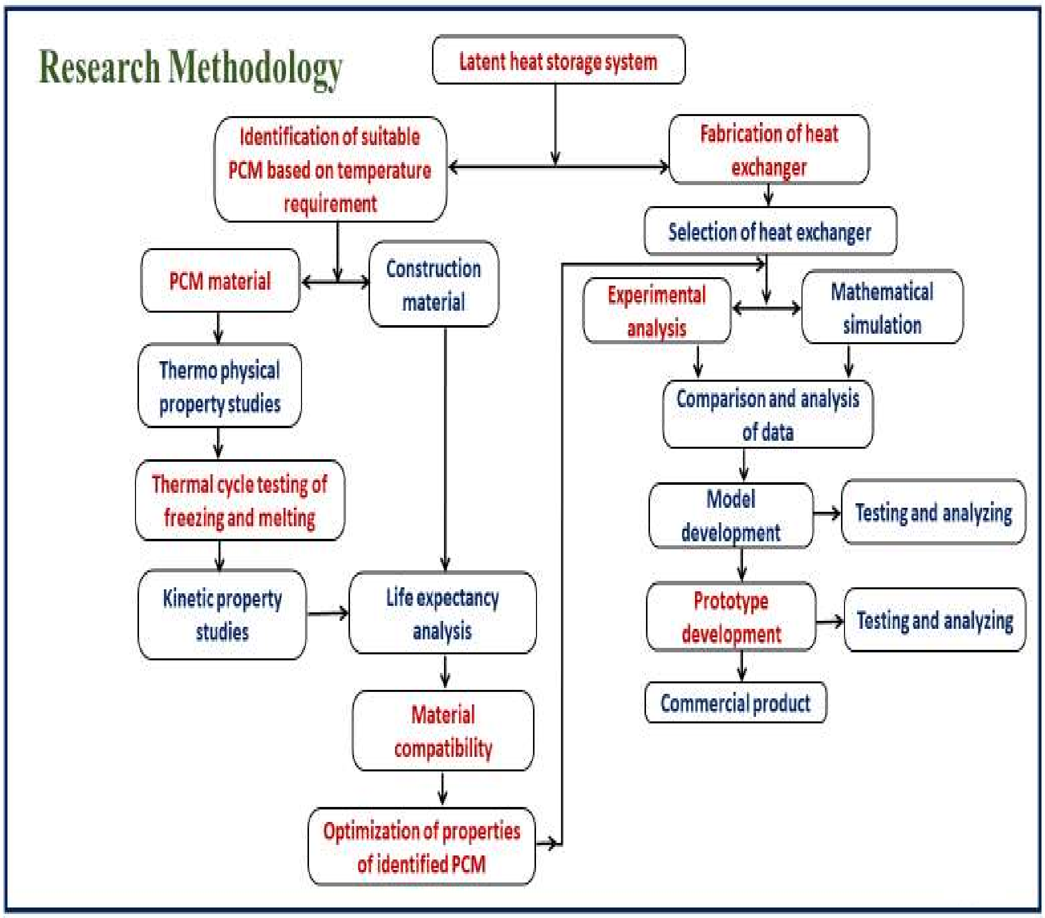


Figure 3.4: Methodology of thermal energy storage (TES) system

First of all investigation on the thermal reliability, chemical stability and corrosion characteristics of the identified material will be done. Then, the said material will be explored as the PCM in a “shell-and-tube system for solar thermal latent heat energy storage” applications. The “thermal behavior” and “heat transfer characteristics of the shell-and-tube type system” will be analyzed during charging and discharging processes. The “changes in melting temperature and latent heat of fusion” of the material will be analyzed above 1000 thermal cycles.

The sample will then be explored as a heat transfer fluid (HTF) in a shell and tube based solar thermal latent heat storage system. The thermal charging and discharging durations for different mass flow rates of the HTF will be obtained at 80 ºC and 25 ºC temperatures, respectively.
It is observed after review of literatures that the PEG-4000 could show promising characteristics of an organic PCM for the "shell and tube based solar thermal latent heat energy storage" applications.

3.4. How the Research Gap is filled?

This research addresses several critical gaps in energy storage technologies by leveraging novel materials, innovative methodologies, and sustainable practices.

The following aspects highlight how these gaps are effectively bridged:

- **Energy and Power Density Trade-Off:**
  - Traditional batteries offer high energy density but struggle with high-power applications, while capacitors excel in power density but lack the capacity for long-term energy storage.
  - The developed supercapacitor, using activated carbon derived from Parali biomass, provides a balanced solution by achieving both high energy density (54 Wh/kg) and high power density (up to 10,000 W/kg). This combination enables the device to cater to diverse applications, including renewable energy systems and portable electronics.
- **Environmental and Resource Challenges:**
  - The widespread use of non-renewable resources in conventional batteries poses environmental and sustainability concerns. By utilizing agricultural waste like Parali, this research offers an eco-friendly alternative that reduces pollution and promotes waste-to-energy practices.
  - The development of PEG-4000-based TES systems further supports environmental goals by integrating renewable energy storage solutions, reducing dependency on fossil fuels.
- **Thermal Energy Storage Efficiency:**

- Existing TES systems suffer from low efficiency and thermal degradation over time. This research introduces PEG-4000, a PCM with high latent heat and thermal stability, ensuring consistent heat storage and release.
- The optimized shell-and-tube heat exchanger design enhances heat transfer efficiency, addressing the limitations of traditional TES systems.

➢ **Scalability and Practicality:**

- Advanced material characterization and simulation-based optimization ensure that the developed systems are scalable and adaptable to real-world applications.
- The research focuses on cost-effective solutions, making the technologies accessible for widespread adoption in sectors like agriculture, energy, and industry.

By integrating novel materials, advanced engineering, and sustainability principles, this research effectively bridges the identified gaps, paving the way for innovative and impactful energy storage technologies.

3.5. Methodology Standards

The Methods in the Research are as per standards to carry out experimental work. The methodologies employed in this research adhere to rigorous scientific standards, ensuring reliability, reproducibility, and validity of the results:

➢ Material Synthesis and Characterization:

- Chemical Activation Process: The use of activation agents (KOH and H_3PO_4) for synthesizing activated carbon follows established protocols in material science, ensuring consistent enhancement of porosity and surface area. The characterization techniques, including XRD, FESEM, BET, and EDS, are industry-standard methods widely accepted for analyzing structural, morphological, and elemental properties of materials.
- Thermal Cycling and Corrosion Testing: The thermal properties of PEG-4000 are evaluated using standard tools like Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), ensuring accurate measurements of phase change behaviour and decomposition temperatures. Corrosion tests follow

ASTM (American society for testing and materials) standards for evaluating material compatibility with the heat exchanger design.

- Device Fabrication and Testing:
  - Supercapacitor Fabrication: The electrode preparation process uses standard material formulations, including binders (PVDF) and conductive additives, ensuring optimal performance. Electrochemical testing methods such as Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) are internationally recognized for evaluating energy storage devices.
  - TES System Development: The design of the shell-and-tube heat exchanger is based on established engineering principles, optimizing parameters like flow rates, material selection, and geometric configurations to ensure efficiency and durability.
- Simulation and Optimization: MATLAB-Simulink Modelling: Simulation of supercapacitor performance and thermal energy storage systems is carried out using MATLAB-Simulink, a trusted platform for modelling and optimization in engineering research. The models are validated against experimental results, ensuring their accuracy and relevance.
- Design Validation: The optimization of design parameters, such as electrode thickness, electrolyte composition, and heat exchanger dimensions, follows standard engineering practices, ensuring scalability and real-world applicability.
- Compliance with Ethical and Environmental Standards: The use of Parali biomass addresses environmental concerns while adhering to ethical practices in waste management and sustainability. Experimental processes minimize chemical waste and ensure safe handling of materials, aligning with laboratory safety standards.

By adhering to these standards, the research achieves a high level of scientific integrity, ensuring that the methodologies and results are credible, impactful, and ready for industrial translation.

3.6. Conclusion of Methodology

The methodology adopted in this research combines experimental rigor, advanced material characterization, and simulation-based optimization to achieve innovative energy storage solutions. Key conclusions from the methodology include:

- **Systematic Development of Materials:**
  - The use of Parali biomass as a precursor for activated carbon demonstrates a sustainable approach to material synthesis, addressing both energy storage and environmental challenges.
  - The characterization techniques confirm the high quality and performance potential of the synthesized materials, ensuring reliability and efficiency in their applications.
- **Comprehensive Device Fabrication:**
  - The supercapacitor design effectively balances energy and power densities, while the TES system demonstrates high thermal efficiency and long-term reliability.
  - The fabrication processes are meticulously documented, ensuring reproducibility and scalability.
- **Simulation for Performance Optimization:**
  - The integration of MATLAB-Simulink modelling allows for a detailed understanding of the effects of various design parameters, enabling the optimization of device performance.
  - Simulation results provide valuable insights that guide the refinement of material properties and device configurations.

The methodology not only achieves the research objectives but also establishes a foundation for future advancements in energy storage technologies, contributing to global sustainability goals.

Chapter 4. Modelling and Simulation

4.1. Simulation based modelling

This chapter belongs to the first objective achievement: "**To model and simulate an existing model with respect to reviews to anticipate and obtain the best possible material, method, and parameter combination**"

The objective is to achieve conclusion about the various parameters and their effects on the performance of supercapacitor device as a whole and to get to know the value range of those parameters to been kept in mind while fabricating the actual device.

Simulation is the process of modelling a device and detecting some variables on which the output of the device most likely to depend. It is done various software and programs available and devices are chosen, and their variable parameters are implemented on the model fed or designed on the software obeying the mathematical equations by which that device is governed. In this way a number of experiments are done to come to conclusion that which parameters are dominantly affecting its performance, and which are not that much relevant.

Using the mathematical equations and equivalent circuit model available for the device, the device can be modelled on a software that suits best in that regard and on the basis of number of simulations some conclusion are generated regarding the actual tangible fabrication of that device and this saves a lot of time and effort and is very convenient too. Now a days before fabrication of any device or system researchers do these kinds of pre-model hypothetical testing and then go for actual fabrication.

Initially a pre-tested supercapacitor has been simulated here for different parameters values and the results have been tabulated for reference as a relationship with the working of the device. Some of the parameters are known from the data sheet of the capacitor in test and some are obtained by screening test and rest a few are adjusted on the MATLAB-environment to optimize the model under observation. From a number of models of supercapacitor available, the best updated model till date has been modelled here in the paper along with the model parameters to get best results. The parameters available with the device are: capacitance, voltage, charging and discharging current ranges.

To optimize the performance, the device must charge itself as fast as possible and discharge itself as slow as possible. Thus, maximum terminal voltage should reach soon after providing the charging current of known range and should delay in discharging when load is connected. The value of total capacitance (C') and total terminal voltage (v) of the device are known by the data sheet of the device provided by the manufacturer. The parameters obtained after testing that can be verified mathematically are shunt capacitance value (C_p), main capacitance value (C), initial voltage (u), charging current value (I) and load value (L). The parameters that can be adjusted during simulation to optimize the results, are chosen from the range of those parameters obtained from different reference papers and are shunt capacitance (C_p), Equivalent series resistance ($ESR=R_1$), self-discharge resistance ($R_{dis}=R_2$), over-voltage protection resistance (R_3), charging (t_c) and discharging time (t_d), simulation time (t_s). Also point to be noted that in this modelling paper of supercapacitor, different combination of values of variables from the ranges of parameters are tried and tested to obtain the best model till date, to obtain best optimized model of the device hypothetically to get a glimpse of effects of these variables on the performance of our device and to help in the making of the device as whole[47-53].

A number of software are available to pre-test the performance affecting dominant parameters of the supercapacitor and they are OrCad, Simulink-Matlab, power-systems, Dymola, Simscape, etc. In this way using a software for modelling the device will provide optimization pathway to have best possible results after the actual device finalization and thus this methodology is called modelling and optimization. A review on these software out of which the best will be used in the case of supercapacitor and are they reliable or not is given in the review chapter coming next[47-53].

As compared with the model simulated on OrCad, direct results are shown below in the picture of OrCad simulated model as follows [47]

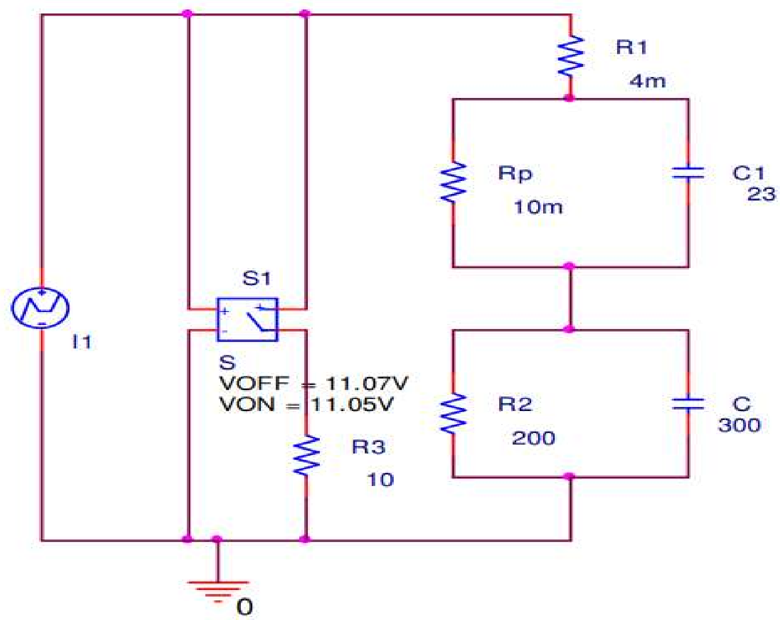


Figure 4.1: OrCad simulated results of a model of Supercapacitor in previous work[47]

From the calculation given in [47], it shows that the ESR (R1) value comes out to be 2 mΩ instead of 4 mΩ as shown in above pictorial result.

The calculation are as follows for the OrCad simulation:

ESR or R1 = dV/I = (11.062 – 11.042)V/10A = 2 mΩ [47].

This value is double what was obtained in simulation [47], which suggest some discrepancy in this simulation platform.

So, we did the simulation for the same as well other model of supercapacitor on Matlab. The output of our Matlab simulations are given in above figures as screenshots.

The supercapacitor to be modelled is EPCOS ESSP48 42V 33F with 18 cells in series and the simulation is done on MATLAB-Simulink environment. This simulation is done similar to another model being simulated on another software[47].

The best equivalent circuit available till now is series parallel RC circuit with nonlinear variables as shown below. This model can be seen from the figures 4.1 & 4.2.

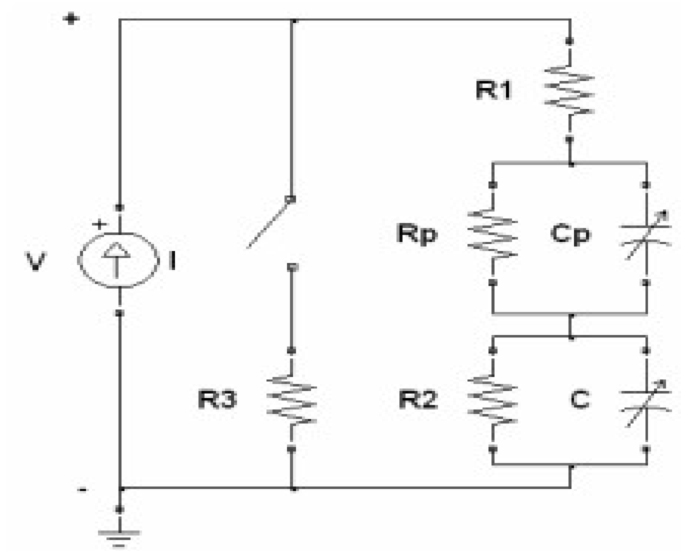


Figure 4.2: Series parallel equivalent cicruit model of supercapacitor with non-linear parameters[47].

Table 4.1: Variable/Modelling parameters

Parameter	**Definition**	**Type**	**Comments**
Total Capacitance (C')	As per the manufacturer	Fixed for a given capacitor	Needs to be high
Cell voltage (v)	Cell voltage	Low	Needs to be high
Current (I)	For charging the capacitor	As per the requirement	To be low
Charging time (t_c)	Time for charging	As per need	To be low
Discharging time (t_d)	Time for full discharging	As per need	To be high
Self-discharge (T_{dis})	Discharging when on no load	A major drawback, high	Needs to be low
Specific capacitance (C)	As per fabrication	Main factor	Needs to be high
Power density (P)	Capacity to take high power load	Generally high	Needs to be high or atleast as it is
Energy density (E)	**Capacity to take load for long duration**	**Generally low**	**Needs to be increased**

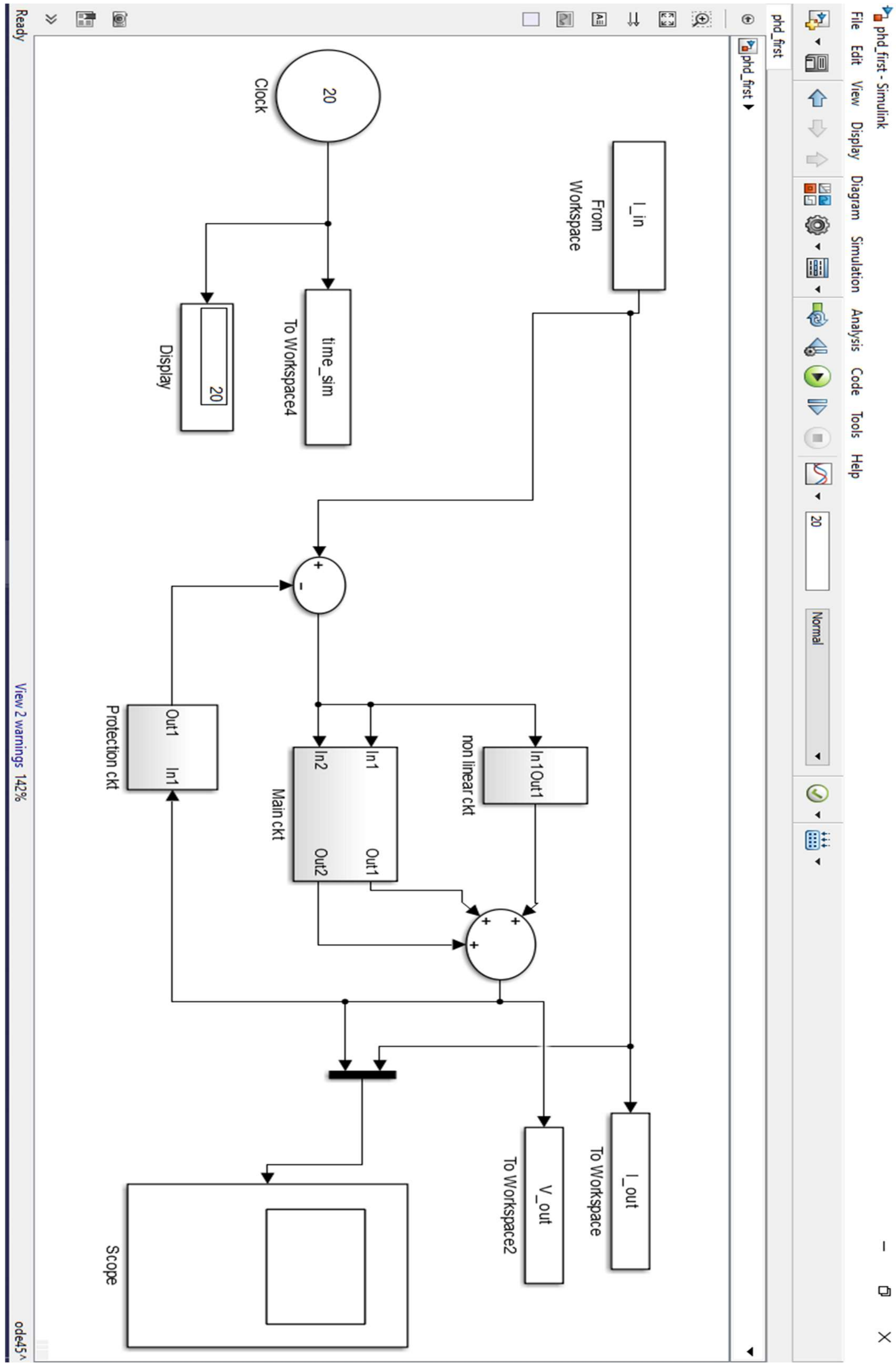


Figure 4.3: Complete Matlab model consisting all the three sub-circuits namely main ckt, non-linear ckt and protection ckt with charging current being 10 A.

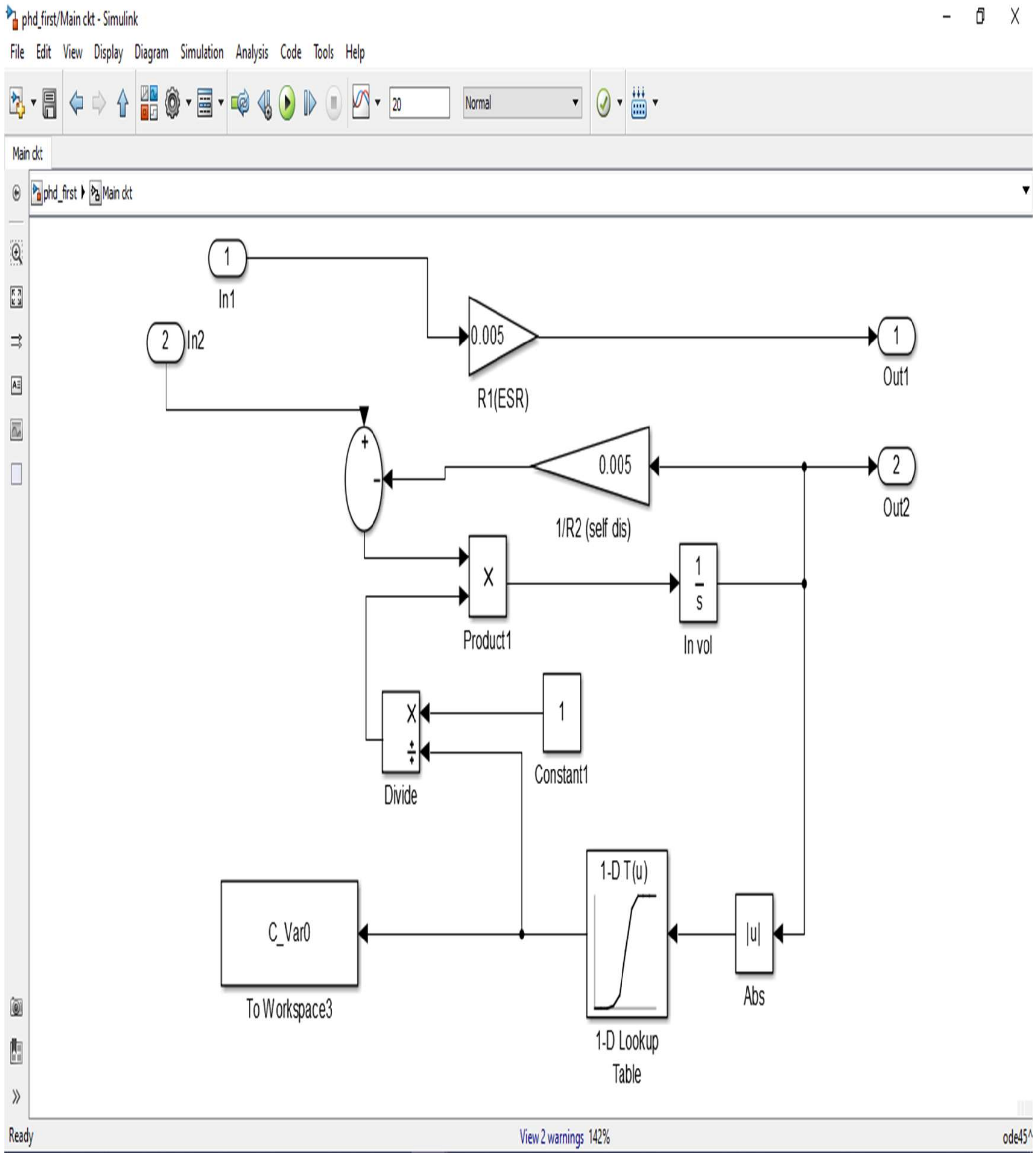


Figure 4.4: Main circuit with ESR and self discharge resistance shown

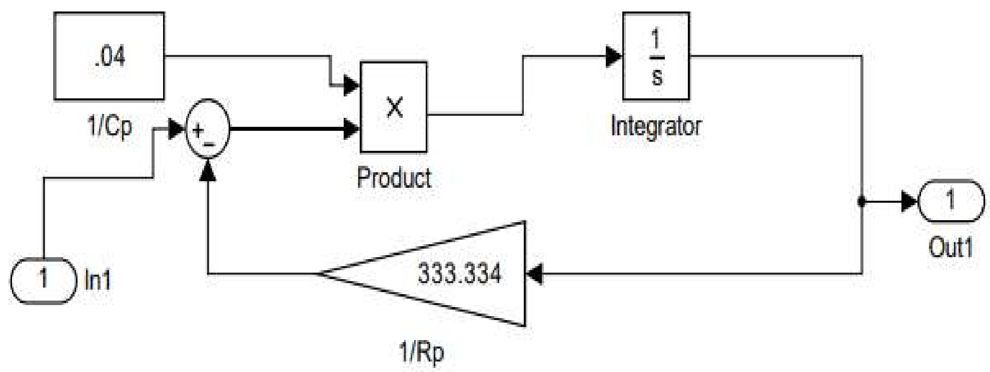


Figure 4.5: Dynamic components of the main circuit that come into existence during operation

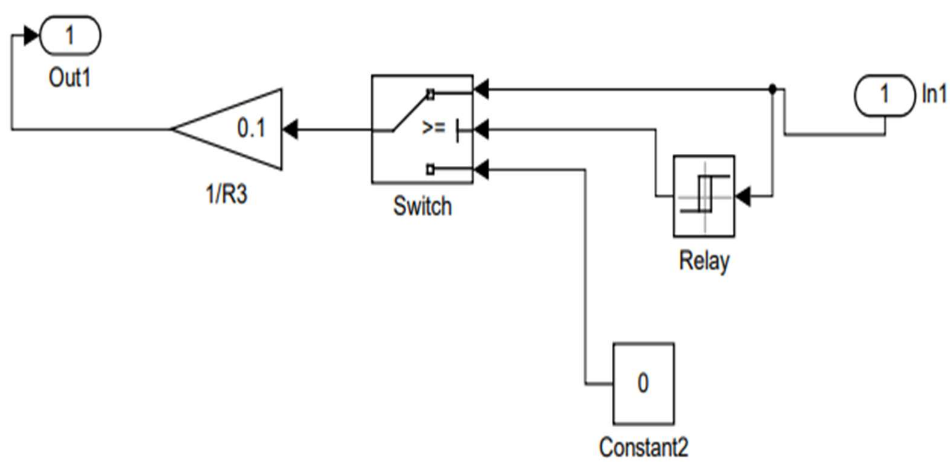


Figure 4.6: Protection or auxiliary circuit which is need required during operation since supercapacitor stops charging automatically when fully charged.

4.2. Results and Discussions

The following graphs belong to the stages of simulation and optimization of supercapacitor device on Matlab: (Figures 4.7 & 4.8)

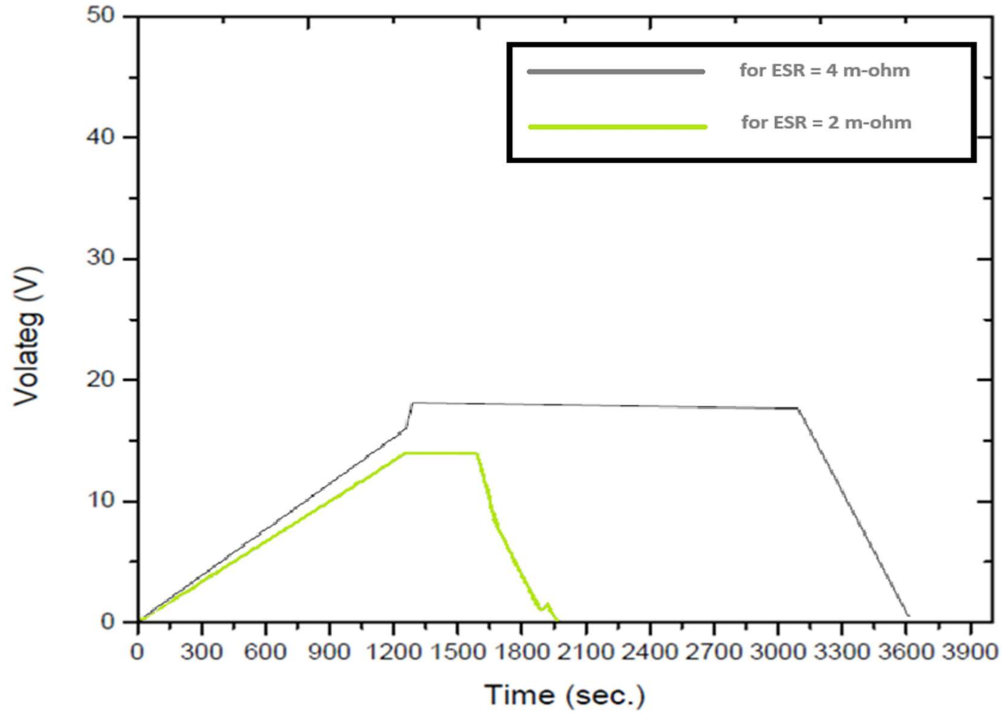


Figure 4.7: “Matlab simulation output for ESR = 2 & 4 mΩ”

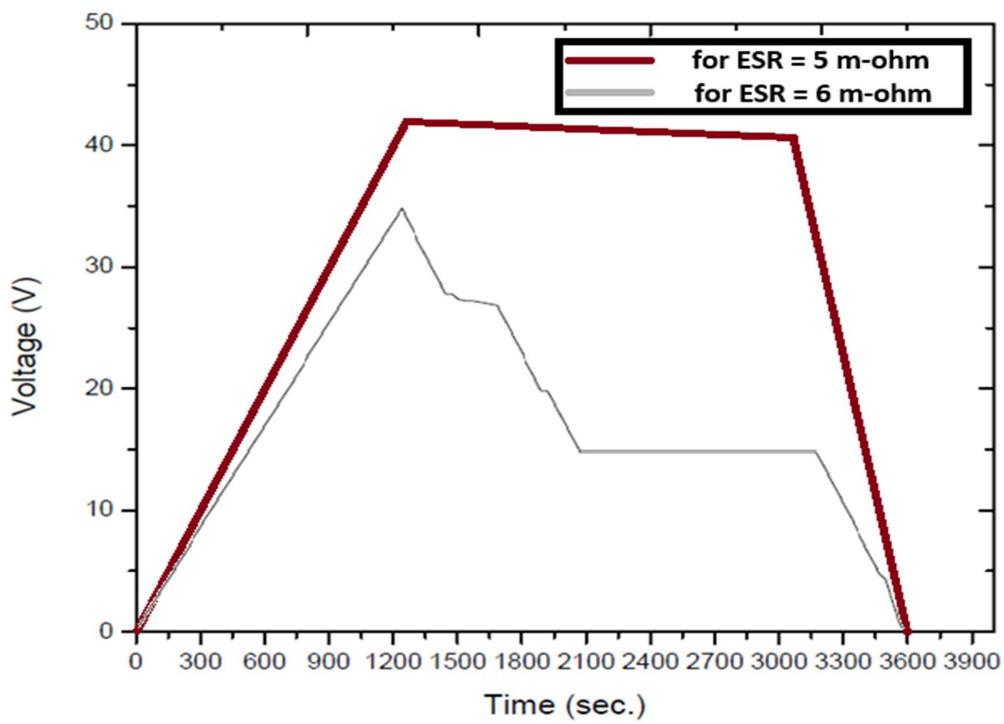


Figure 4.8: “Matlab simulation output for ESR = 5 & 6 mΩ”

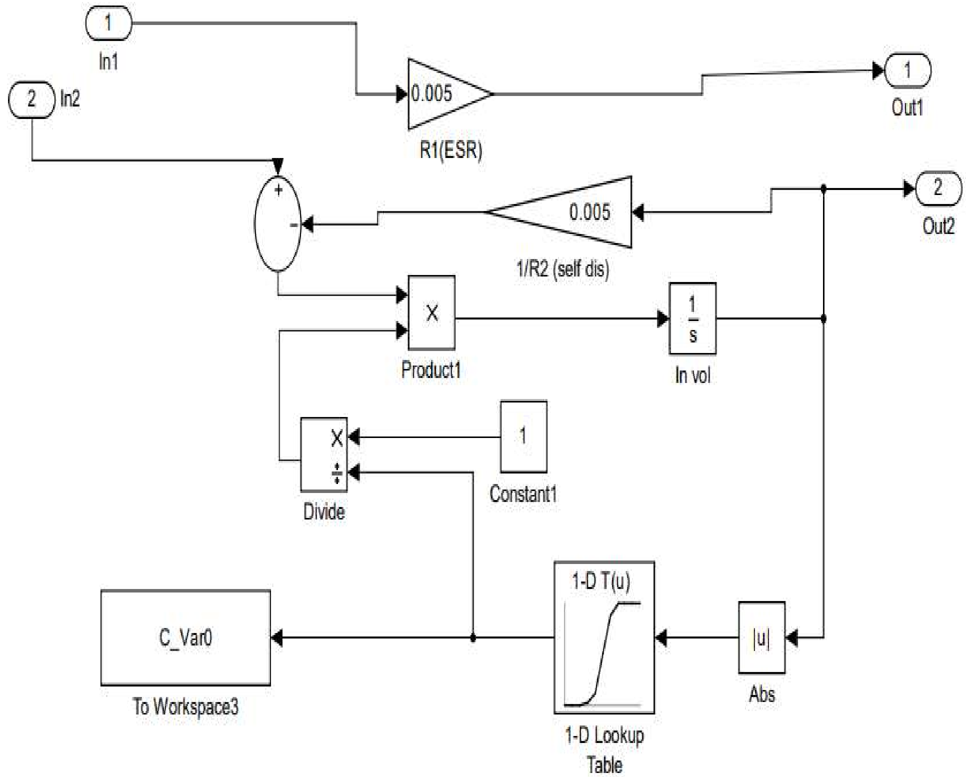


Figure 4.9: Optimized main circuit >> ESR or R1 = 5 mΩ

The value of ESR has been varied from in the range of upto 1-10 mΩ [28]. The optimized results were obtained at ESR being 5 mΩ, which indicates that optimized ESR value which majorly depends on electrode, will yield high charge storage capacity and longer duration discharging i.e. high energy density. The various simulation outputs are presented as obtained from the Simulink work flow.

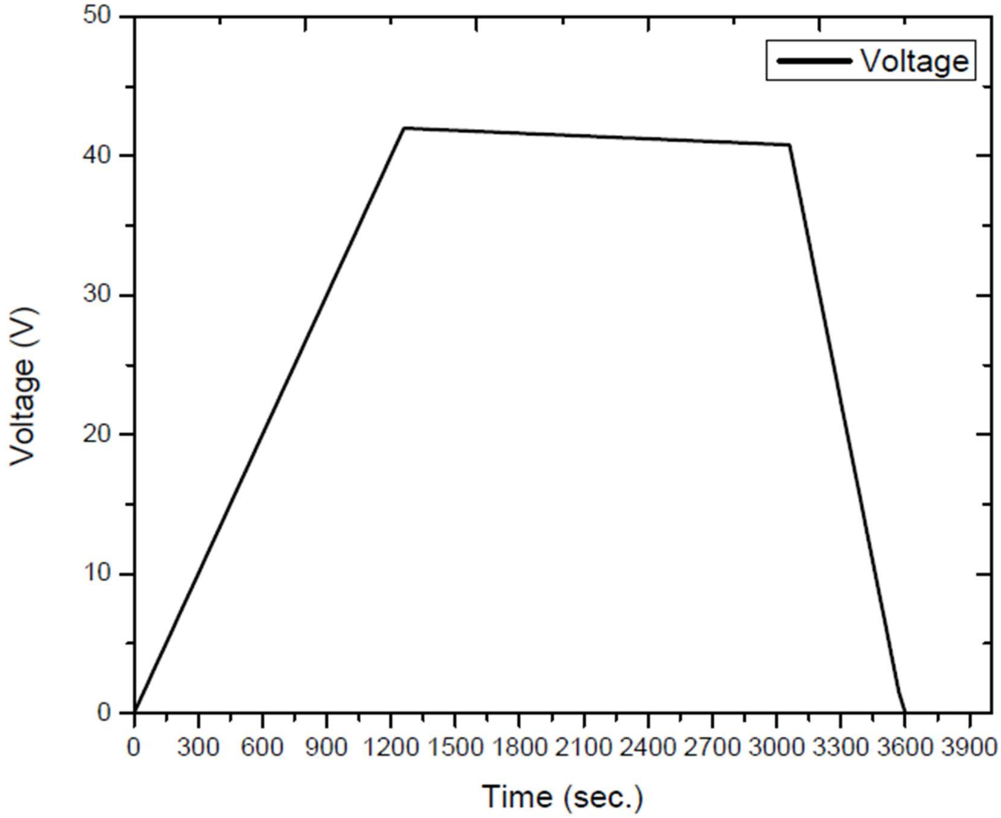


Figure 4.10: Final optimized extracted output with ESR 5 mΩ

So, it can be concluded that although a different model of supercapacitor was modelled and simulated here in Matlab environment, and voltage being 3 times. What the observation says that a minor variation in the resistance of the electrode can remarkably decrease the charging time and increase the energy density (supplying same load after reduced charging time) as shown in the table. The goal of the project will be to have similar symmetric graphs at output during electrochemical testing of electrodes of supercapacitor and have maximum specific surface area and minimum resistance which will ultimate pave way for high energy density during load supply.

Table 4.2: Comparative results of modelling and simulation

	Previous work[47]	This work	Remarks
Software	OrCad	Matlab	Different software for simulation as Matlab is better of all[47-53]
Model	ECOND Pscap350	EPCOS Essp48	Various models of supercapacitor exist[47-53]
Voltage	14 V	42 V **(3 times)**	It means for charging and discharging it should take triple the time period
Charging current	10 A	10 A	Kept same for comparison. *(Should take triple time to full charge)*
Charging time	7 minutes (for full 14 V charging ***(@ 2V /min.)***	21 minutes to full charge of 42V ***(@ 2V/min.)***	Charging takes 3 times as the voltage is 3 times. *Correct simulation on the way.*
Self-discharge Resistance	200Ω	200Ω	Self-discharge circuit is also kept same for easy comparison
Current cut-off period *(= shelf time)*	10 minutes (= 600 sec.)	30 minutes (= 1800 sec.)	Left with zero current supply for triple period to compare the self-discharge.
Self-discharge *(It varies from 1-2 days for discharge [28])*	0.6V/h *(= 1 day for full discharge)*	0.2V/h *(= 1.75 days full discharge)*	Improved *i.e. slow self-discharge So if a supercapacitor with higher voltage is designed using series cells then self-discharge can be remarkably removed.*
Discharging/ load current	-20 A	-20 A	Kept same for comparison. *(Should supply the same load for triple time longer)*
ESR or R1 *(majorly depends material of electrodes)*	**4mΩ** (OrCad Simulation results) but **2mΩ** by calculation. ***(Mismatch)***	**5mΩ optimized** *(varied from 1-10 mΩ [28])*	**So at most optimized ESR value, the self-discharge, discharge time, and energy density were all optimized.** *This indicates that electrode material and fabrication process play a vital role.*
Discharging time	2 minutes (= 120 sec.) ***(@ 7V/min)***	10 minutes (= 600 sec.) ***(@ 4.2V/min)***	Very symmetrical and supplies load 5 times instead of 3 times. ***Energy density*** *is improved since same load is supplied for longer duration than expected.*

Chapter 5. Experimental Details

5.1. Introduction to Experimental Works of the Research

The experimental phase of this research represents the core of its innovative approach, focusing on the synthesis, fabrication, and evaluation of novel energy storage systems. Key components include:

- **Material Development and Characterization:**
  - Parali biomass is chemically activated using agents like KOH and H3PO4 to produce high-quality activated carbon.
  - The materials undergo comprehensive characterization to determine properties such as surface area, porosity, and elemental composition. Techniques like XRD, BET, FESEM, and EDS play a critical role in validating the quality and performance potential of the synthesized materials.
- **Supercapacitor Fabrication:**
  - Electrodes are prepared by mixing the activated carbon with binders and conductive additives, forming a composite material with optimal properties for energy storage.
  - A coin-cell configuration is used for the prototype, ensuring a compact design and ease of testing.
- **TES System Development:**
  - PEG-4000 is selected as the Phase Change Material for its superior thermal properties.
  - A shell-and-tube heat exchanger is designed to optimize heat transfer and storage capabilities, addressing the limitations of existing TES systems.
- **Performance Testing:**
  - The supercapacitor undergoes electrochemical testing, including CV, GCD, and EIS, to evaluate energy density, power density, and stability.
  - The TES system is subjected to thermal cycling and corrosion tests to ensure long-term reliability and efficiency.

This experimental phase lays the foundation for achieving the research objectives, demonstrating the feasibility and scalability of the proposed systems.

5.2. Electrical Energy Storage (EES): Parali Supercapacitor (Device 1)

5.2.1. Material Characterization

Parali biomass undergoes a series of steps to produce Parali Carbon (PC), a fine black non-activated carbon powder.

Initially, the biomass is collected and cleaned, then ground to obtain a rough powder. Subsequently, it undergoes pre-carbonization at 180°C for 2 hours without combustion. The resulting material is pulverized into a fine powder and cleaned with distilled water, acetone, and 1M HCl to eliminate impurities. Next, the activation process begins.

Three grams of PC is activated using a mixture of 3-15 grams of KOH and H_3PO_4 in different weight ratios of 1:1, 1:3, 1:5 etc. resulting in different types of parali-activated carbons: PAC1xK (activated with KOH) and PAC1xH (activated with H_3PO_4), where x represents activation agent mass ratio with respect to carbon sample mass.

Activation occurs at 600°C for 6 hours under a Nitrogen environment in a muffle furnace. The activated samples are washed with 1M HCl and distilled water multiple times to remove any remaining impurities before being dried at 105°C for 2 hours in air. Not all the pictures have been put to avoid confusion.

Figure 5.1: Showing different mass ratio mixing of carbon sample with activation agents

Once the samples are prepared, they undergo characterization before proceeding to electrode preparation. The characterization includes XRD analysis to detect graphitic carbon presence, Energy Dispersive Spectroscopy (EDS) to determine the carbon percentage, and FESEM analysis to examine structural morphology, porosity, and crystallinity. Additionally, the BET technique is employed to quantify porosity, calculate average pore diameter, and measure specific surface area. Figures 5.1 and 5.2 illustrates the steps involved in sample preparation.

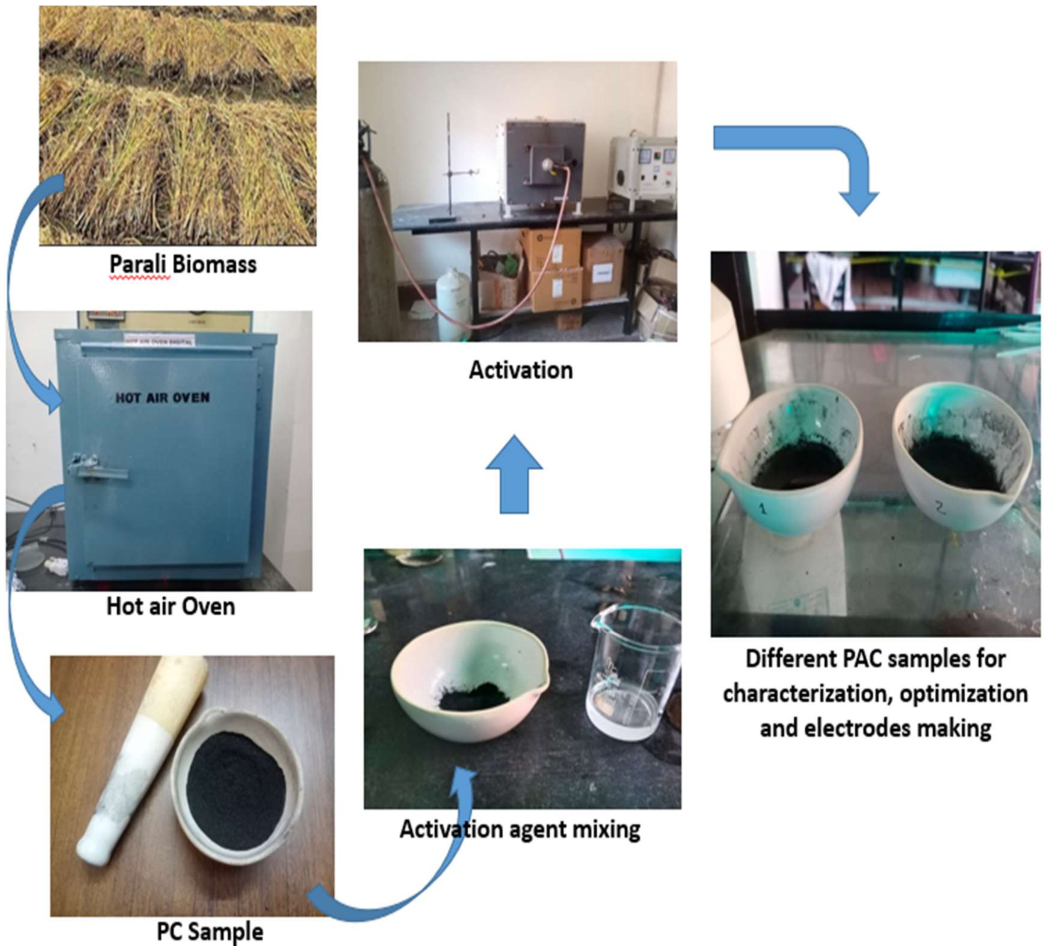


Figure 5.2: Steps utilized to prepare the samples of activated carbons with KOH and H_3PO_4

5.2.2. Supercapacitor Device Fabrication

Once material characterization is complete for both activated and non-activated carbon, electrodes are fabricated using most optimized sample having the highest specific surface area obtained after BET analyses of all samples. The electrodes are then meticulously characterized and optimized for supercapacitor electrochemical performance using an electrochemical workstation comprising a Cyclic Voltammeter (CV) and Galvanometric Charge-Discharge (GCD) system. Supercapacitor investigation involving these electrodes encompasses both non-activated and activated carbon, initially rendered conductive via a three-electrode setup. This setup comprises the working electrode (activated/non-activated carbon), counter electrode (platinum wire), and reference electrode (Silver/silver chloride, Ag/AgCl), all submerged in a 6M KOH electrolyte. The preparation of working electrodes involves blending carbon material "(activated and non-activated, each 80% by weight), Carbon black (10% by weight), and Polyvinylidene fluoride (PVDF, 10% by weight)". PVDF serves as a binder, ensuring adherence of the main material to the substrate, namely Ni-Foam/mesh, which also acts as the substrate and current collector. Carbon black functions as both a conductive agent and filler material in the process, also known as Acetylene black. "N-methyl-2-pyrrolidone (NMP)" is utilized as solvent which help to form a homogenous "slurry" of the mixture, which is then cast onto the Ni-Foam (1x1 cm^2 area, 0.5 mm thickness) using the dip-casting method. After overnight drying, the electrodes are further dried the next day in a hot air oven at 80°C for 4 hours. The total mass loading of the electrode is determined by subtracting the mass of the unloaded Ni-foam substrate from the mass of the Ni-foam loaded with carbon material. Subsequent analyses are conducted using a "three-electrode setup in a 6M KOH electrolyte". The whole procedures can be observed from the figures that follow.

Figure 5.3: Showing 80:10:10 ratio by mass mixing of Sample with PVDF and carbon black (CB) respectively to make the final sample ready for electrode preparation.

NMP is used to make slurry during electrode casting on Ni-foam. Following the above pathway, a number of electrodes were made, of which the figures are given below.

Figure 5.4: Showing the preliminary stages of electrodes fabrication

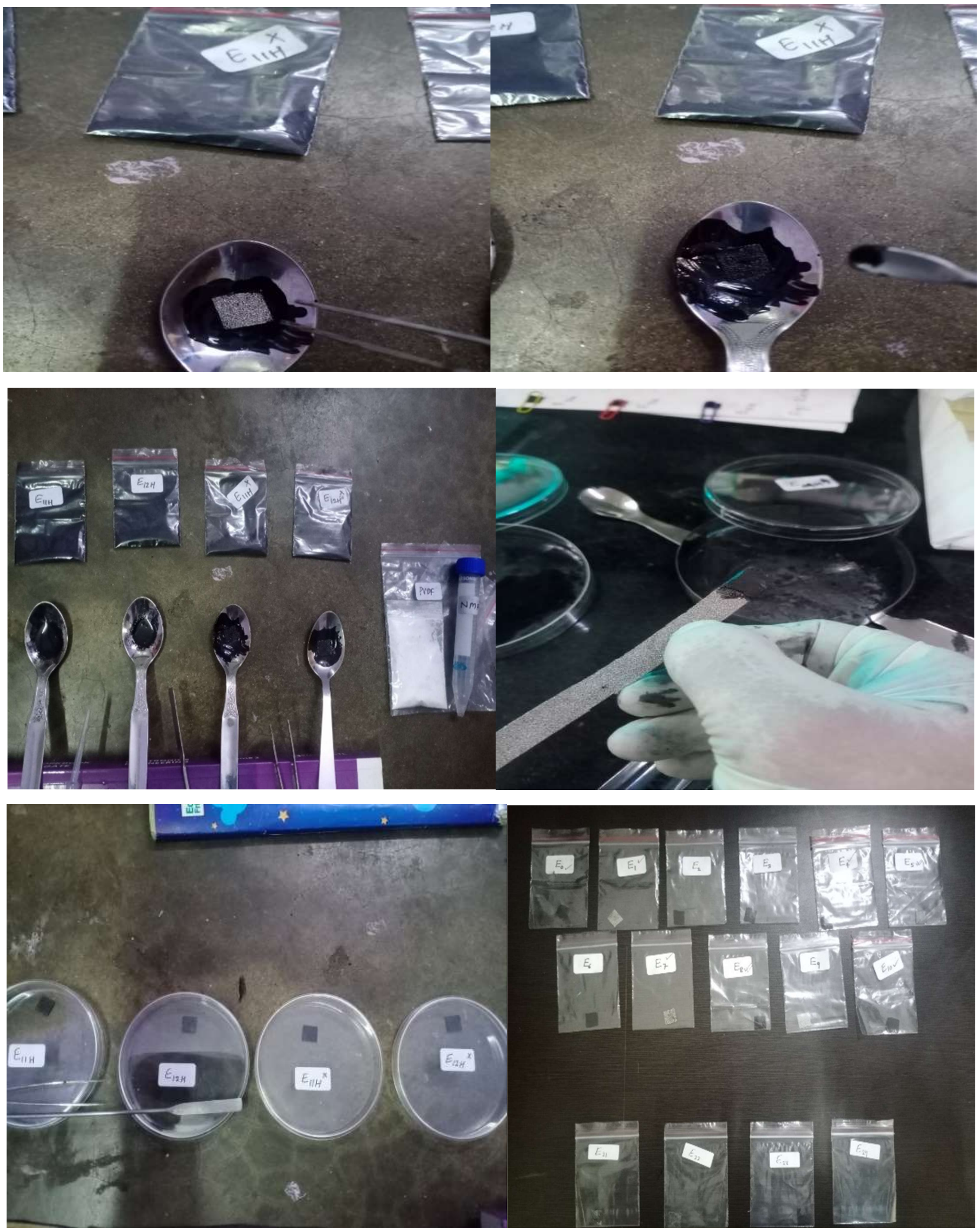


Figure 5.5: Showing the final stages of electrodes fabrication

After various electrodes have been made from the optimized and best carbon sample (highest specific surface area activated carbon), they have been characterized and tested and optimized under three-electrode configuration on electrochemical work station for the device fabrication.

Figure 5.6: Showing the setups of electrode testing and characterization

After the results obtained for best electrode, the device was fabricated and characterized under two-electrode configuration (laboratory proto-type device) for performance for load supply and "specific capacitance and energy density" determination as the final stage of electrical energy storage system fabrication and analyses. After the results of each and every electrode fabricated from optimized carbon samples (PC, PACK and PACH), the device was fabricated and tested for loads as the figures follows.

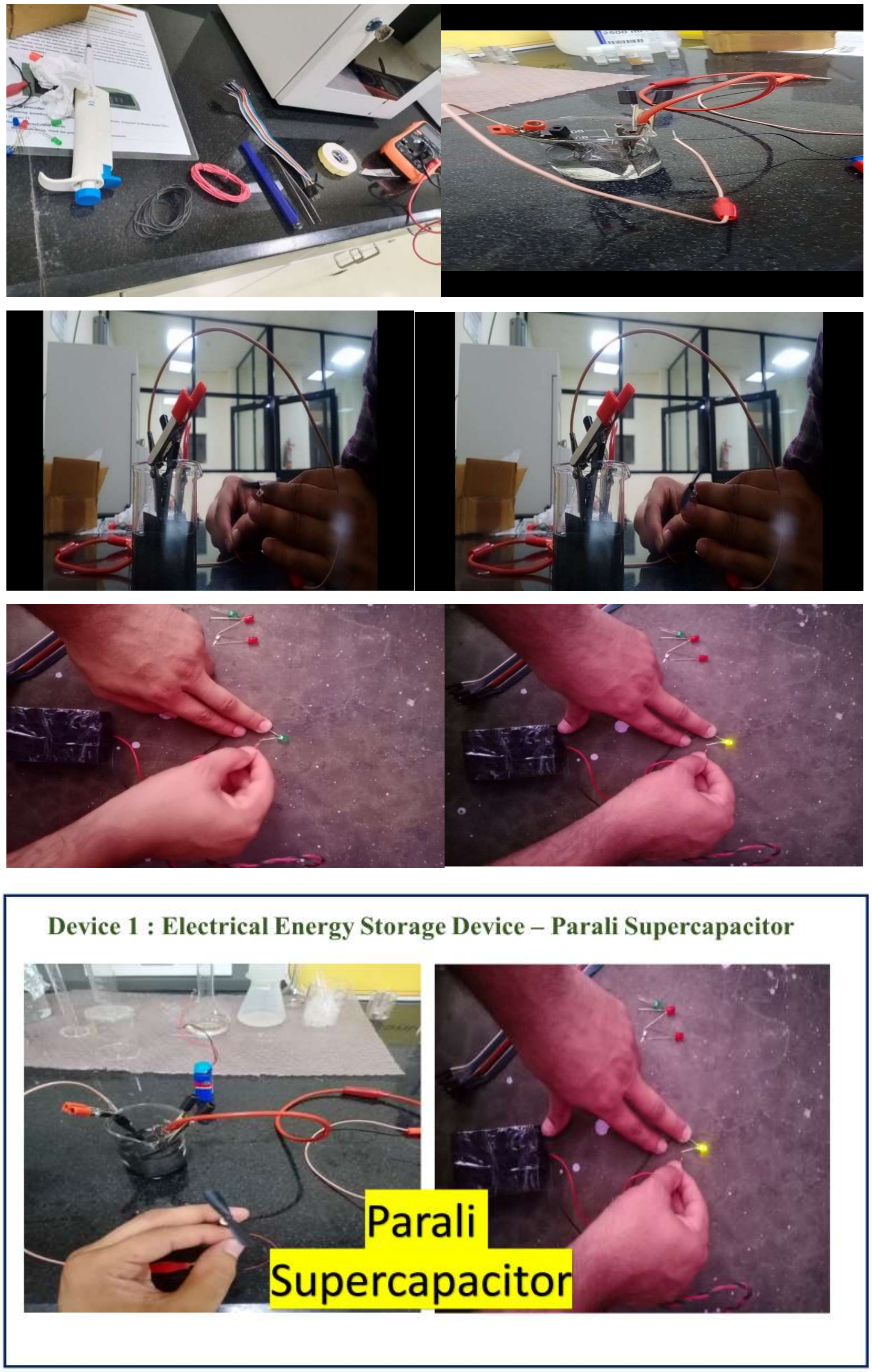


Figure 5.7: Fabricated Device 1 (EES) running LED and dc motor loads successfully

5.3. Thermal Energy Storage (TES): Heat Exchanger (Device 2)

5.3.1. Material Characterization

An experimental investigation is undertaken to identify suitable organic Phase Change Materials (PCM) for "Thermal Energy Storage (TES)". The primary objective of this study is to examine the impact of one thousand accelerated thermal cycles on the "Latent Heat of Fusion (LHF)" and melting temperature of "PEG-4000". Furthermore, the study delves into assessing the compatibility of PEG-4000 with stainless steel, copper, and aluminium, considering their potential as container materials for medium-temperature storage applications.

PEG 4000, a non-paraffin organic PCM with 98% purity, is procured from Sisco Research Laboratories (SRL) Pvt Ltd., India. An "Accelerated Thermal Cycling Test" is conducted using a thermal cycler to analyse the "thermo-physical properties" such as LHF and phase change temperature of PEG 4000. In this procedure, 20g of PCM is filled into a test tube and placed in a hot bath maintained at 80°C for the charging process until complete melting occurs, followed by cooling in a cold bath at 10°C until solidification is achieved. PEG-4000 is subjected to one thousand melting and freezing cycles. Samples of approximately 1 gm are extracted at regular intervals of every 100 cycles to measure their thermo-physical properties, including "Phase transition temperature" and "Latent heat of fusion", utilizing a Differential Scanning Calorimeter (TA- Q20 DSC) operating between 0 to 80°C at a temperature ramp of 10°C/min.

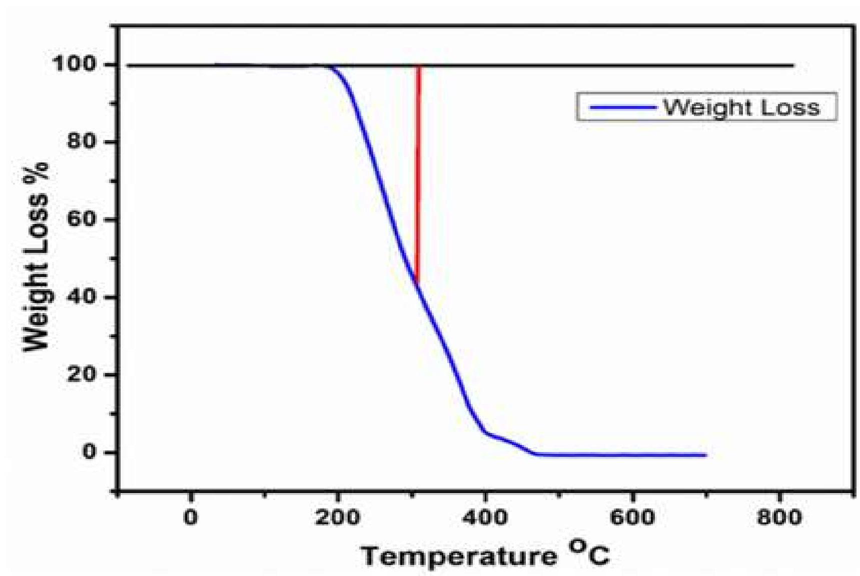
Additionally, the thermal stability of PEG-4000 PCM is assessed using a Thermogravimetric Analyzer (TGA instrument, TA Instruments—Q600 SDT) at a heating rate of 10°C/min under a constant stream of N_2. The chemical stability of PEG 4000 after thermal charging and discharging cycles is examined via "Fourier Transform Infrared (FTIR) spectroscopy" using "Thermo Nicolet 6700" equipment, with a scan range spanning from 4000 to 400 cm^{-1}.

In next step, the corrosion behaviour of PEG 4000 in contact with various container materials, namely "Copper (Cu), Aluminium (Al), and Stainless Steel (SS 304)", is examined. Test samples measuring 10 mm in width and 30 mm in length are utilized for this investigation. The metal specimens undergo a thorough cleaning process with ethanol and acetone for 10 minutes and are then subjected to a hot air oven at 80°C for an additional 10 minutes to eliminate impurities and moisture. Subsequently, each of the three metal samples is individually placed in separate test tubes and fully immersed in PEG-4000 PCM. These samples undergo heating and cooling for one thousand thermal cycles. Following the thermal cycling, the metal samples are removed from the test tubes and cleaned with acetone and ethanol. They are then dried in a hot air oven at 80°C for ten minutes to eliminate residual moisture. The final weight of each metal sample is measured to assess any changes. The corrosive impact of PEG-4000 PCM on the three metal samples is evaluated by calculating the percentage mass/weight loss observed in each case.

Weight loss	"Recommendation"
> 50%	"Destroyed within days"
10-50%	"Not recommended for service greater than a month"
5-10%	"Not recommended for service greater than one year"
1-5%	"Caution recommended, based on the specific application"
0.5-1%	"**Recommended** for long term service"
<0.5%	"**Recommended** for long term service; nearly no corrosion"

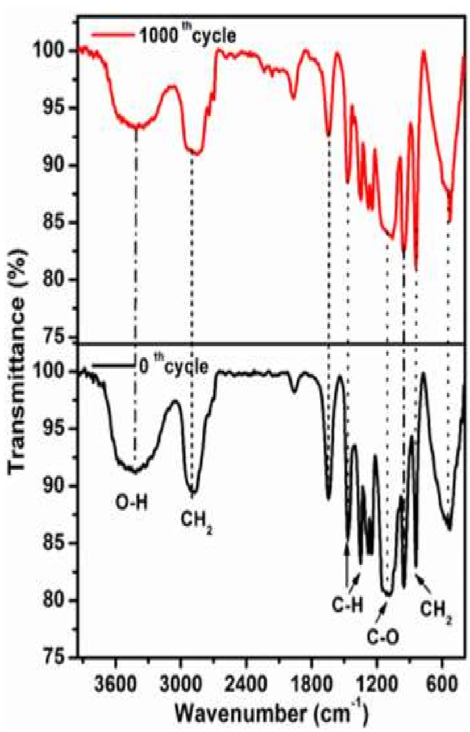
Figure 5.8: Industry standards of 3 container materials for corrosion

Thermal stability studies of PEG 4000



TGA curve of pure PEG 4000

Figure 5.9: TGA spectrum of pure PEG-4000 PCM sample



FTIR spectra of 0th and 1000th cycle of PEG 4000

Figure 5.10: Chemical Stability studies of PEG-4000

Table 5.1: Properties of PCM (Phase change material)

Phase change material	**Polyethylene Glycol (PEG-4000)**
Phase transition temperature (°C)	58 – 60
Specific heat (kJ/kg K)	1.74
Latent heat capacity (kJ/kg)	150.8
Thermal conductivity (W/mK)	0.25
Density (g/cm^3)	1.09

Table 5.2: Properties of heat transfer fluid (HTF)

Fluid	**Therm 500**
Operating temperature	Upto 300 °C
Vapor pressure	0.05 bar
Specific heat	2.058 kJ/kg K
Thermal conductivity	0.1179 W/mK
Density	952.2 kg/m^3

5.3.2 Parameters to Design Heat Exchanger

The design of the shell-and-tube heat exchanger is guided by a set of critical parameters, ensuring optimal performance and durability:

- **Thermal Properties of PEG-4000:**
  - The PCM's high latent heat (146 J/g) and thermal stability are key factors in achieving efficient heat storage and release.
  - Thermal cycling tests confirm that PEG-4000 retains its properties over extended periods, ensuring long-term reliability.
- **Flow Rate Optimization:**
  - The heat transfer fluid (HTF) flow rate significantly influences the charging and discharging efficiency. Experiments reveal that flow rates of 3–5 kg/min during charging and 2–3 kg/min during discharging provide the best results.
- **Material Selection:**
  - Stainless steel is chosen for its corrosion resistance and durability, ensuring compatibility with PEG-4000 and the HTF.

- Tube diameter and wall thickness are optimized to balance heat transfer efficiency and material costs.

➢ **Geometric Considerations:**

- The number of tubes, their arrangement within the shell, and the overall shell dimensions are designed to maximize heat transfer surface area while minimizing thermal losses.

By carefully optimizing these parameters, the heat exchanger achieves high thermal efficiency and reliability, making it suitable for renewable energy applications.

5.3.3 Heat Exchanger Device Fabrication

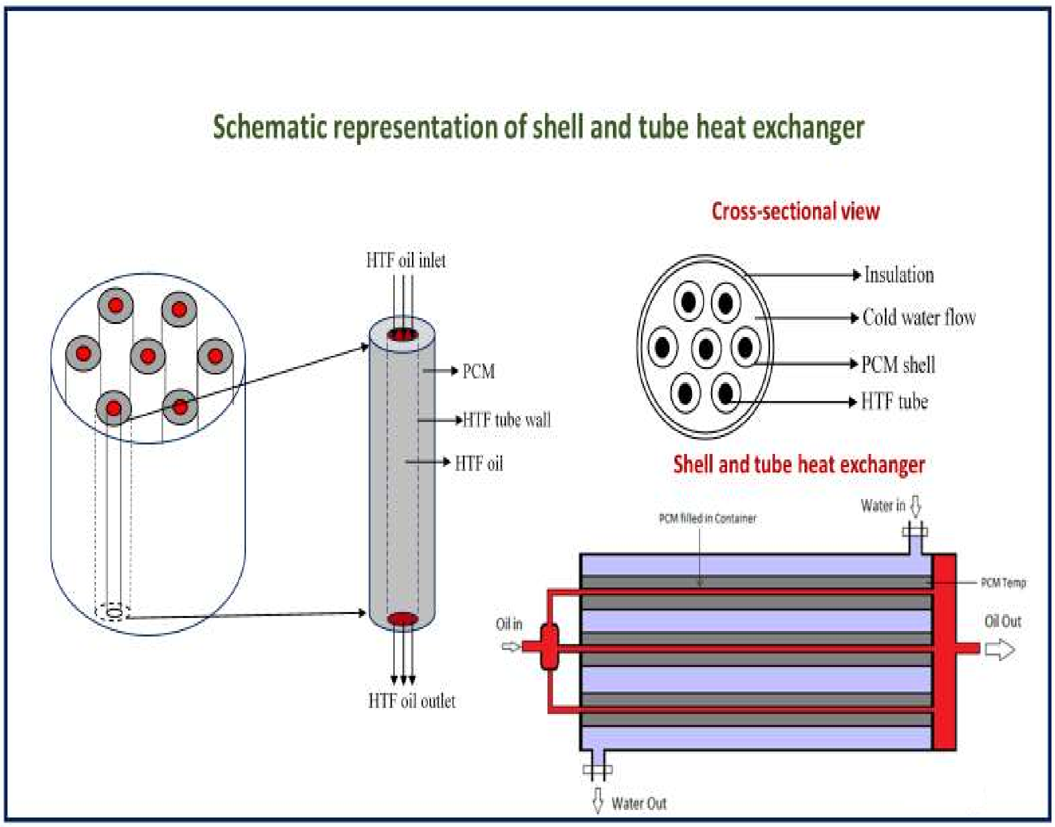


Figure 5.11: Schematic of Shell-tube heat exchanger

Table 5.3: Geometry of shell and tube heat exchanger

Dimensions of inner tube (HTF tube)	Inner tube material	Copper
	Inner diameter of inner tube (HTF tube)	16 mm
	Outer diameter of inner tube (HTF tube)	17 mm
	Thickness of inner tube (HTF tube)	1 mm
	Length of inner tube (HTF tube)	500 mm
Dimensions of shell (PCM)	Outer shell material	Copper
	Inner diameter of shell (PCM)	70 mm
	Outer diameter of shell (PCM)	72 mm
	Thickness of shell (PCM)	2 mm
	Length of shell (PCM)	500 mm
Outer enclosure shell	Outer shell material	Stainless steel
	Inner diameter of outer shell	260 mm
	outer diameter of outer shell	261mm
	Length of outer shell	500 mm
Insulation	Material	Ceramic wool
	Thickness	30 mm

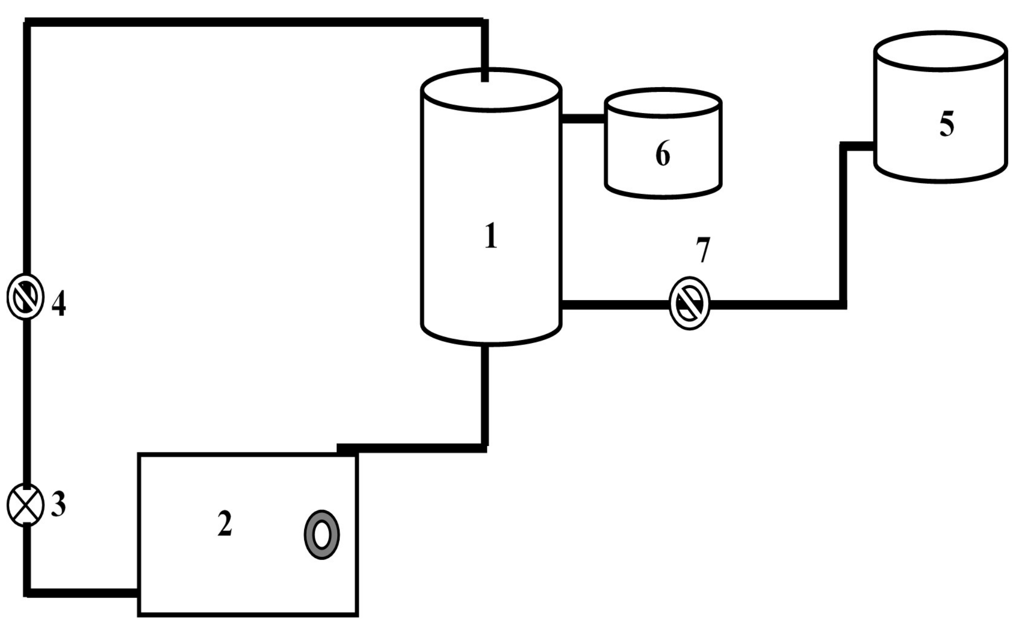


Figure 5.12: Schematic representation of experimental test setup

The latent heat thermal energy storage experimental test loop consists of

(1) PCM heat exchanger,

(2) Temperature controlled thermostatic oil bath,

(3) External gear pump,

(4 and 7) Flow control valve,

(5) Cold water storage tank and

(6) Hot water storage tank and K-type thermocouples with data acquisition system.

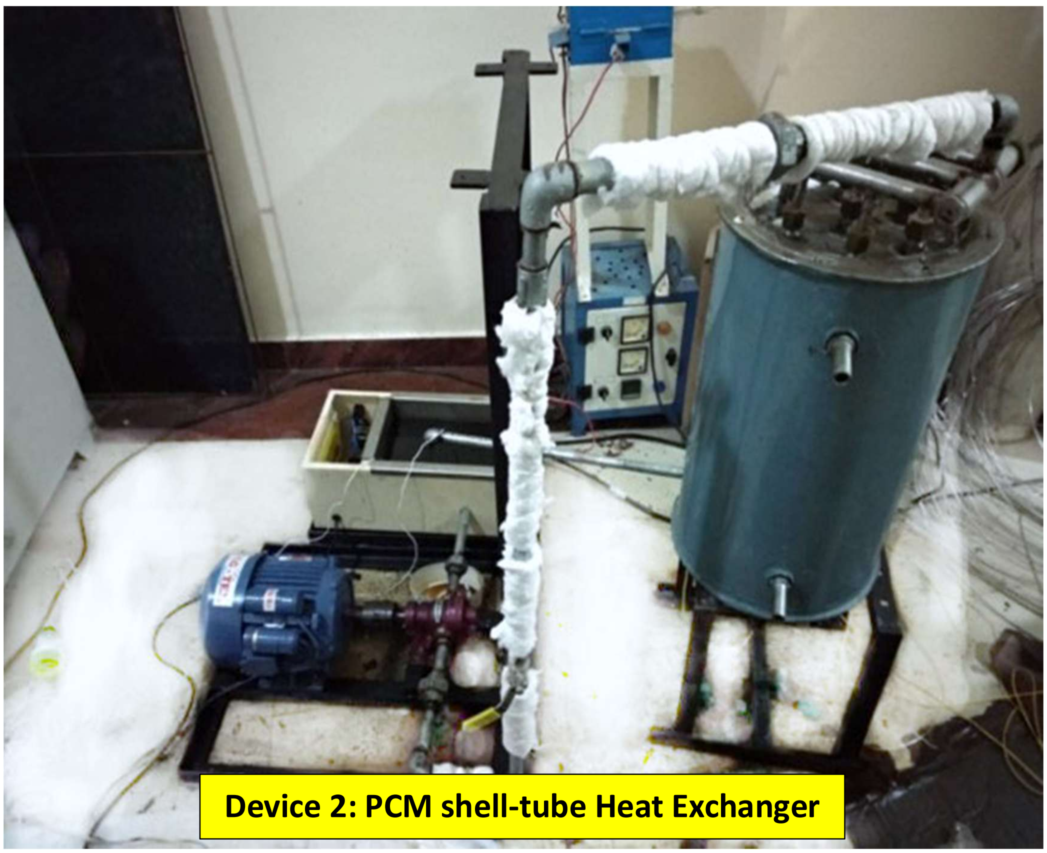


Figure 5.13: Fabricated Device 2 (TES) heating water successfully

Researchers who study heat exchangers are particularly interested in how the speed of the heat transfer fluid (HTF) circulation affects the overall heating performance of a liquid heating system (LHS). The LHS itself is made up of several parts, such as the heat exchanger itself, an oil bath, a pump that controls the flow externally, valves to regulate flow, tanks for storing hot and cold water (labelled 4, 5, 6, and 7 in Figure 5.12), and a special temperature sensor (K-type thermocouple) connected to a data logging system for recording measurements. The PCM heat exchanger system primarily comprises cylindrical tubes constructed from copper, standing at a height of 350mm. These tubes feature an inner diameter of 60mm for the PCM shell and 15mm for the Heat Transfer Fluid (HTF) tube. The PCM is situated between the shell and HTF tube. Table 5.3 presents the dimensions of the shell and tube PCM heat exchanger. This shell and tube configuration are housed within an enclosure crafted from stainless steel, boasting an inner diameter of 250 mm. To minimize heat loss, the heat exchanger is insulated using ceramic wool, which has a thickness of 25 mm. Figure 5.13 depicts the "PCM shell and tube heat exchanger".

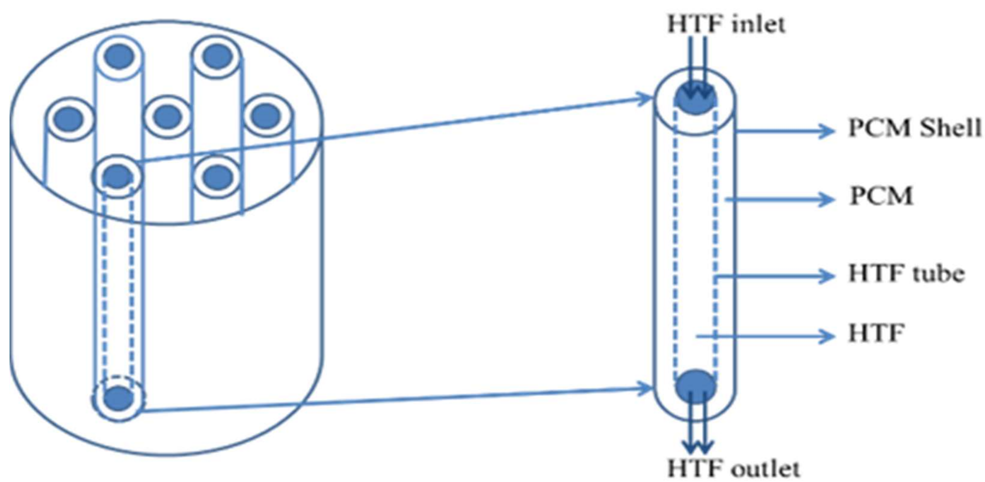


Figure 5.14: "Schematic diagram of shell and tube heat exchanger"

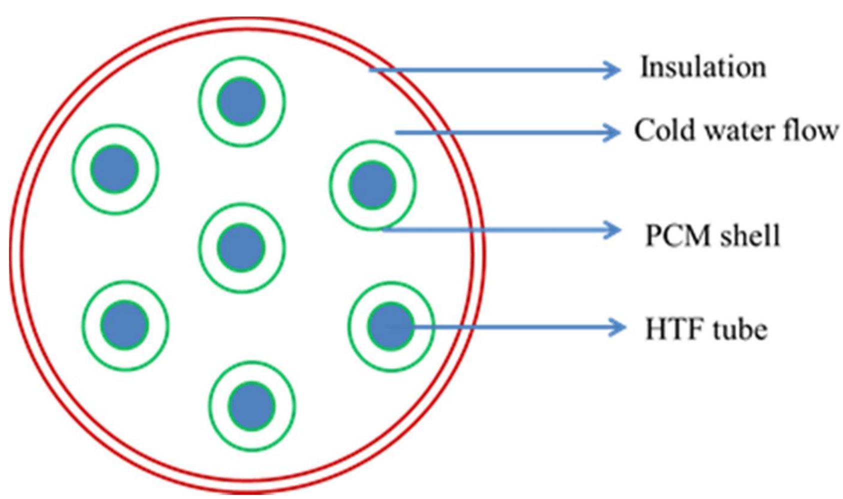


Figure 5.15: Cross Sectional view of shell and Tube Heat Exchanger

Technical grade Poly Ethylene Glycol (PEG) serves as the Phase Change Material (PCM) due to its thermal reliability, chemical stability, and low corrosiveness, even after undergoing 1000 cycles of charging and discharging. The PCM heat exchanger is loaded with 2 kg of PEG 4000. For charging the PCM, Thermic fluid (THERM 500) acts as the Heat Transfer Fluid (HTF). During the melting phase of the PCM, the HTF is heated in an oil bath at a constant temperature and circulated through the HTF tube. The mass flow rate of the HTF is regulated by adjusting the valve connected to the HTF flow loop. Cold water from the storage tank is utilized to extract heat during the discharging process of the PCM.

K-type thermocouples are strategically positioned to measure the temperature of the PCM, as well as the outlet and inlet temperatures of the HTF. Additional thermocouples are placed at the inlet and outlet of the HTF tube to monitor the HTF temperature. All thermocouples are linked to a data logger for temperature recording.

The thermal melting (charging) of the PCM is conducted by varying the mass flow rates of the HTF. Charging experiments are conducted at HTF mass flow rates of 3 kg/min, 4 kg/min, and 6 kg/min until the PCM reaches its phase transition temperature and completely liquefies. Simultaneously, discharging experiments are performed in the heat exchanger. Discharging experiments are carried out under different mass flow rates of water stagnation conditions, namely 4 kg/min and 2.2 kg/min. During the discharging process, heat stored in the PCM is extracted by continuously circulating cold water around the PCM shell until the PCM completely returns to its solid state at room temperature.

5.4. Conclusion to Experimental Works

The experimental studies confirm the feasibility and effectiveness of the proposed energy storage systems.

Key conclusions include:

- **Supercapacitor Performance:**
    - The use of Parali-derived activated carbon results in high specific capacitance (247.6 F/g) and energy density (54 Wh/kg), demonstrating its potential for diverse applications.

- Long-term stability tests validate the durability and efficiency of the device, with minimal performance degradation over 5,000 cycles.

- **TES System Efficiency:**
    - PEG-4000 proves to be an excellent PCM, with consistent phase transition properties and high thermal reliability over 1,000 cycles.
    - The shell-and-tube heat exchanger design ensures efficient heat transfer and storage, addressing the limitations of traditional TES systems.

These findings highlight the innovative contributions of this research, paving the way for scalable and sustainable energy storage solutions.

Chapter 6. Results and Discussions

6.1. Introduction to Results and Discussions

The results and discussions chapter provide a detailed analysis of the performance metrics for the developed energy storage systems. Key highlights include:

- **Material Characterization Results:**
  - XRD and BET analyses reveal the structural and textural properties of the activated carbon, confirming high surface area (151.42 m^2/g) and porosity (average pore size: 2–10 nm).
  - FESEM and EDS results validate the effectiveness of chemical activation, showing a significant increase in carbon content and the removal of impurities.
- **Supercapacitor Electrochemical Performance:**
  - CV and GCD tests indicate exceptional energy and power densities, with the device achieving rapid charging and stable performance over multiple cycles.
  - EIS analysis reveals low ESR and high charge transfer efficiency, ensuring optimal performance under varying conditions.
- **TES System Thermal Performance:**
  - The system demonstrates consistent heat storage and release capabilities, with minimal thermal degradation over extended use.
  - The optimized heat exchanger design achieves efficient heat transfer, validated through experimental testing under different flow rates and operating conditions.

These results underscore the success of the proposed methodologies, highlighting their potential for real-world applications.

6.2. Electrical Energy Storage (EES): Parali Supercapacitor (Device 1)

6.2.1. Material Characterization

XRD, FESEM, EDS, and BET analyses were utilized to examine the crystal structure and morphology of the synthesized functional carbons[126].

6.2.1.1 FESEM analysis:

FESEM analysis is conducted to assess the surface morphology of both non-activated and activated carbons PACK and PACH

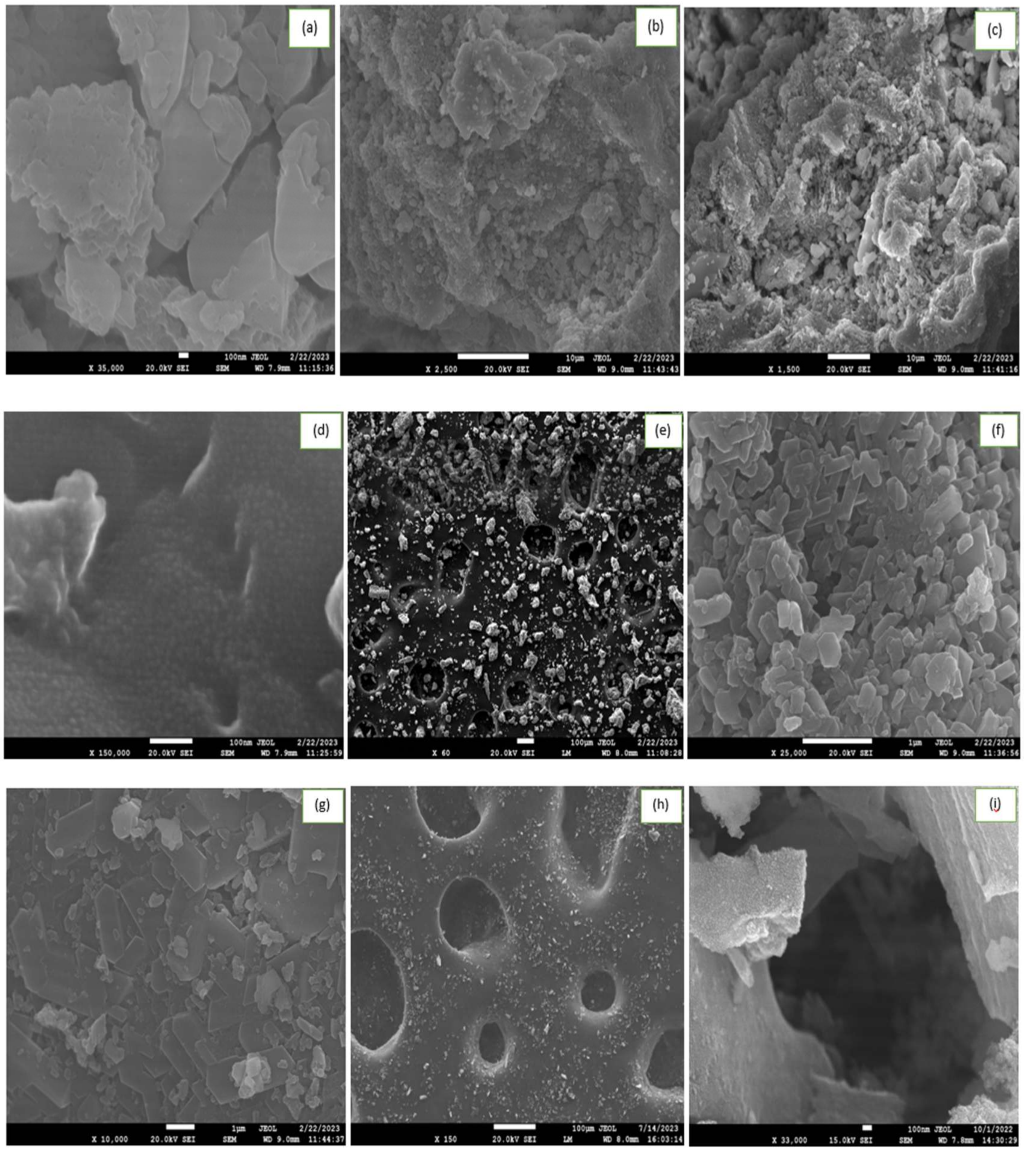


Figure 6.1: (a)-(c): FESEM images of non-activated PC, (d)-(f): KOH-activated PAC and (g)-(i): H_3PO_4-activated PAC

Figures 6.1 (a)-(c) depict FESEM images of the non-activated PC, while Figures 6.1 (d)-(f) showcase KOH-activated PACK and Figures 6.1 (g)-(i) display H_3PO_4-activated PACH carbons.

It is evident from Figure 6.1 that the surface of the non-activated parali carbon appears nearly solid, non-crystalline, and non-porous, characteristics typically associated with low surface area. However, following activation, the carbon becomes porous and crystalline, indicative of an increased surface area. These pores are anticipated to facilitate rapid ion/electron transport during the electrochemical performance evaluation and testing. A lot of FESEM testing (not shown here) on various materials prepared so far show that PACH can be potential candidate. Also, PC and PACK have also been used for electrode fabrication for comparison purpose.

To mention here that a number of samples were made as discussed in the previous experimental chapters, out of which as an initial step all samples were testes for FESEM analyses to observe which one seem potential candidate for to move on with. Here in figures 6.1 all the FESEM results of all samples prepared so far are presented like PC, PAC1xK and PAC1xH. In this way it become easier to determine the best materials and go for further characterization like XRD, EDS and BET analyses.

6.2.1.2 XRD analysis:

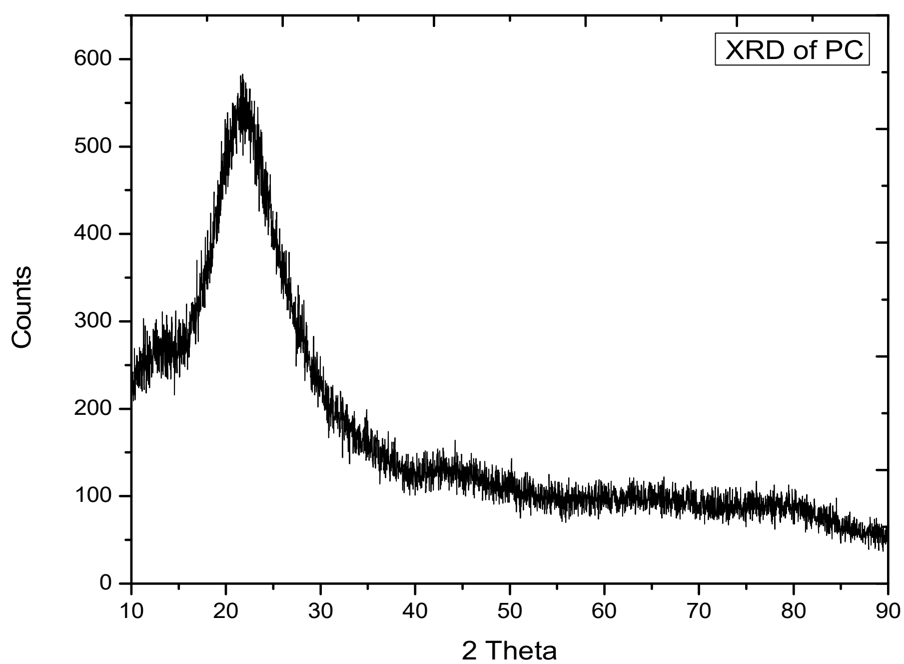


Figure 6.2: XRD of Non-activated carbon called Parali carbon (PC)

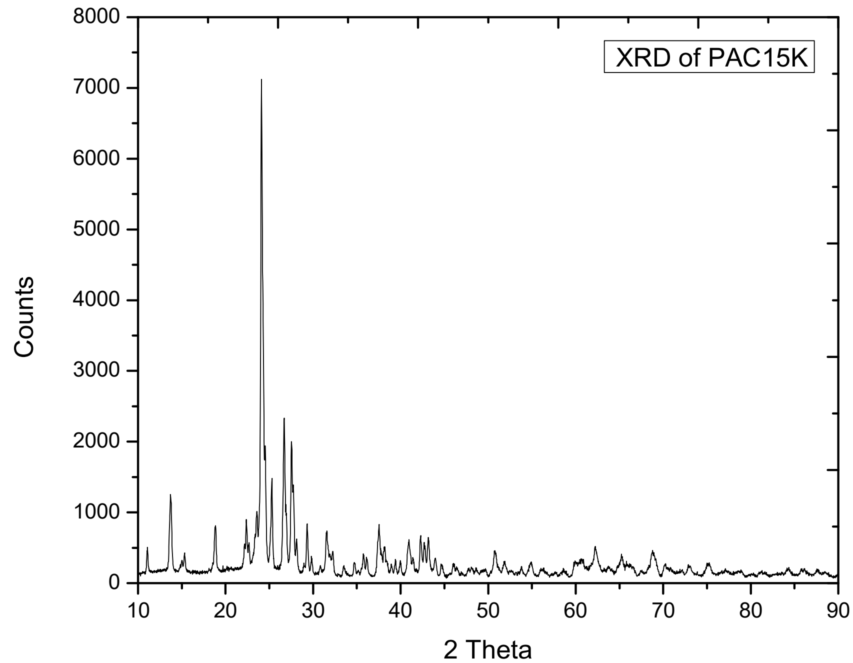


Figure 6.3: XRD of Parali activated carbon with KOH (PACK)

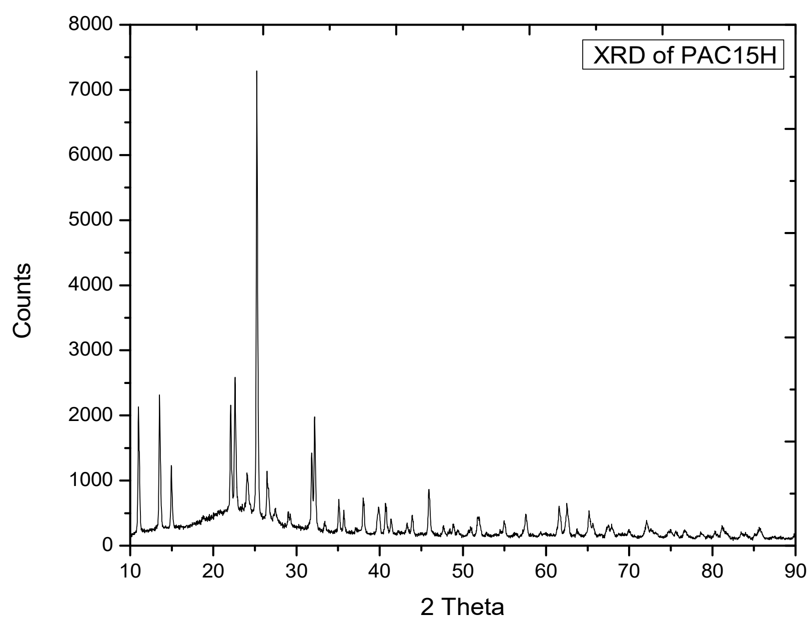


Figure 6.4: XRD of Parali activated carbon with H_3PO_4 (PACH)

Figures 6.2-6.4 illustrates the XRD pattern of PC, PACK and PACH. The Bragg peaks observed at diffraction angles signify the presence of graphitic carbon, affirming its quality as a good useful potential carbon source[126]. It is evident from the XRD curves that PACH is best out of PC and PACK.

6.2.1.3 EDS analysis:

Now for better understanding of how much exact amount of carbon is present in these samples, EDS analyses were carried out.

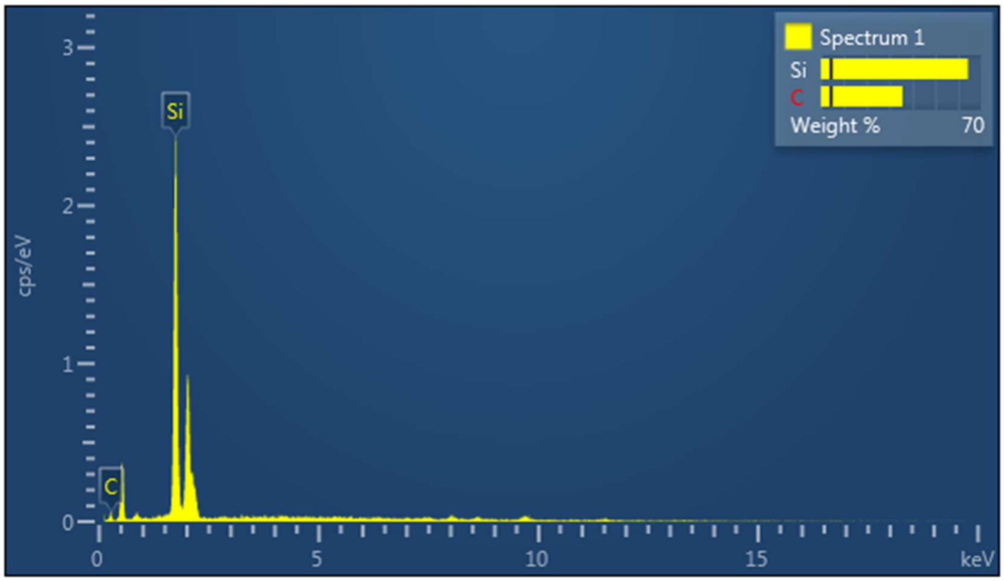


Figure 6.5: EDS of PC

Figure 6.6: EDS of PACK

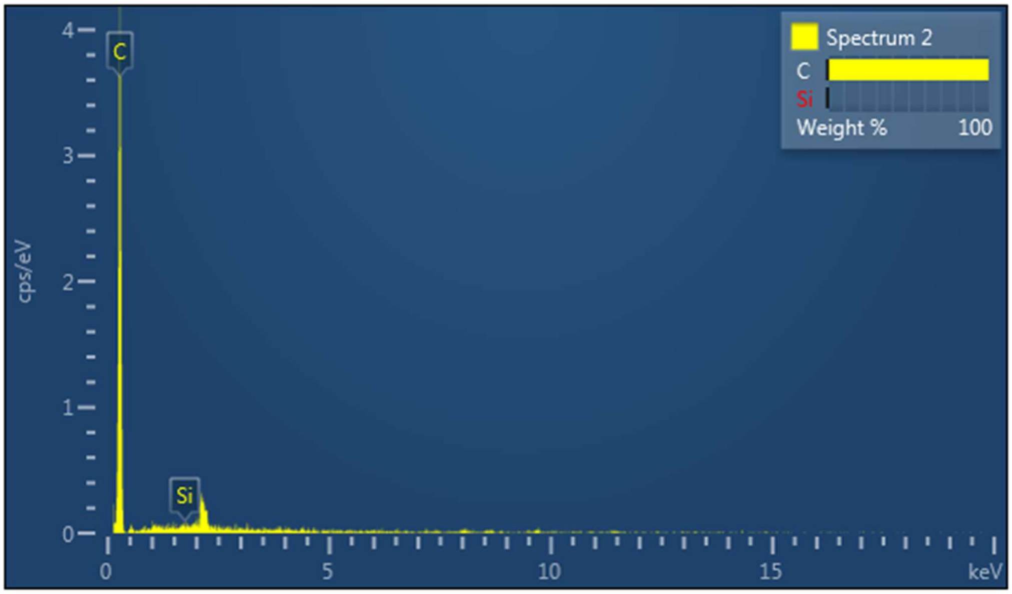


Figure 6.7: EDS of PACH

Table 6.1: Comparison summary of EDS results

Carbon material sample	Carbon content in % [EDS results]	Comments
Non activated Parali carbon i.e. PC	35.71	Very low carbon content as usual in case of biomass due to impurities
PACK	49.55	Best of this group
PACH	**99.85**	**Carbonized/purified remarkably**

Quantitative analysis of carbon content in the samples was conducted for both pre-carbonized and activated carbon utilizing EDS. Table 6.1 illustrates that the carbon content in non-activated parali-derived carbon is notably low at 35.71%, in contrast to the activated samples, which exhibit percentages of 49.95% and 99.85%. The presence of impurities, particularly silicon contamination, is attributed to the industrial area location where the raw parali was collected. However, the activation process has significantly reduced impurities to enhance the material's carbonaceous nature.

Detailed comparative analyses of table 6.1

Table 6.1 compares the Energy Dispersive Spectroscopy (EDS) results for three key materials: non-activated Parali carbon (PC), Parali activated carbon with KOH (PACK), and Parali activated carbon with H_3PO_4 (PACH). These materials were synthesized to evaluate their suitability for supercapacitor applications. The comparison focuses on the elemental composition (primarily carbon and oxygen) and the implications for their performance as electrode materials.

The various elements and their comparative impacts can be tabulated as below:

Table 6.2: Comparative analyses of elements of EDS results

Element	**PC (%)**	**PACK (%)**	**PACH (%)**	**Key Observations**
Carbon (C)	35.71	99.85	98.62	Carbon content increases significantly in activated samples (PACK and PACH), indicating successful activation and removal of impurities. PACK achieves the highest purity.
Oxygen (O)	64.29	0.15	1.38	Oxygen content decreases drastically in activated samples, reflecting the removal of oxygen-containing functional groups. This reduction enhances conductivity and electrochemical performance.
Potassium (K)	-	Trace	-	Trace amounts of K are present in PACK due to residual activation agent (KOH). This contributes to the improved porosity and surface area.
Phosphorus (P)	-	-	Trace	Trace P content in PACH originates from the H_3PO_4 activation process, influencing surface chemistry and pore development.

- Non-Activated Parali Carbon (PC):
  - Carbon Content (35.71%): Raw Parali biomass has a relatively low carbon percentage, indicating that it contains significant amounts of

non-carbon elements (mainly oxygen). This highlights the need for activation to enhance its suitability for energy storage.

- Oxygen Content (64.29%): High oxygen content suggests the presence of oxygen-containing functional groups, which contribute to poor conductivity and limit its effectiveness as an electrode material.

➢ Parali Activated Carbon with KOH (PACK):

- Carbon Content (99.85%): The activation process with KOH drastically improves the carbon content by removing impurities and oxygen-containing groups. This makes PACK highly conductive, enabling better charge storage and transfer.
- Oxygen Content (0.15%): The near-complete removal of oxygen ensures low resistance and high conductivity, critical for supercapacitor applications.
- Potassium (K) Trace Amounts: Residual potassium contributes to the development of a porous structure with a high specific surface area. This enhances the energy storage capacity of the electrode.

➢ Parali Activated Carbon with H_3PO_4 (PACH):

- Carbon Content (98.62%): Activation with H_3PO_4 also significantly enhances carbon content, although slightly less than PACK. The difference may stem from variations in activation efficiency between KOH and H_3PO_4.
- Oxygen Content (1.38%): The residual oxygen content is higher compared to PACK, which may slightly impact its conductivity. However, this oxygen may also introduce beneficial functional groups that enhance pseudocapacitive behaviour.
- Phosphorus (P) Trace Amounts: Phosphorus residues from the activation process can influence surface chemistry, contributing to enhanced electrochemical interactions.

These key elements do have a very good impact on the electrochemical performance required for the supercapacitor device which can be seen as:

- High Carbon Content:
    - PACK's carbon content of 99.85% makes it the most promising candidate for supercapacitor electrodes, as high carbon purity directly correlates with better conductivity and energy storage performance.
    - PACH also performs well, with 98.62% carbon content, making it a strong alternative.
- Low Oxygen Content:
    - The low oxygen content in PACK (0.15%) minimizes resistive losses, making it ideal for applications requiring high power density.
    - PACH's slightly higher oxygen content (1.38%) may provide additional pseudo-capacitance, potentially benefiting applications that require a combination of high energy and power densities.
- Porosity Development:
    - Both PACK and PACH show significant improvements in porosity, as evidenced by their activation agents (KOH and H_3PO_4). This enhances the electrode's specific surface area, enabling greater charge storage.

Hence the results show the impact of chemical activation on the elemental composition of Parali carbon. PACK emerges as the most promising material due to its high carbon content, minimal oxygen presence, and optimal porosity, making it highly suitable for supercapacitor applications. PACH, while slightly less conductive, offers potential benefits through pseudocapacitive effects, making it an excellent complementary material for hybrid energy storage systems.

The findings from table 6.1 validate the effectiveness of Parali biomass activation and underscore its potential as a sustainable, high-performance material for advanced energy storage technologies. It can be seen from the table that functional carbon samples that can be used from each group are PC, PACK and PACH out of which most promising candidate looks to be PACH and when the electrodes making, and testing will be done then only the exact picture will be obtained.

6.2.1.4 BET analysis:

For the BET analyses a selected number of samples were tested for specific surface are and porosity which are the main parameters that affect the charge storage capacity hence the energy density of the electrodes. The BET results are given in below figures and a summary table has also been presented before proceeding to the final conclusion about the best sample carbon.

Note: highest specific surface area is obtained when the pore size is mesoporous i.e. 2-10 nm. This material sample will be further used for designing of different electrodes with different mass loading and studies will be carried out on EWS to calculate their corresponding specific capacitances with the help of GCD curves of each electrodes as well as energy densities.

From all these carbon samples a number of electrodes were made and characterized and optimized. After that, the best electrode from the best material sample was utilized for the making of the laboratory proto-type supercapacitor device. Though PACH is looks most optimized carbon sample which can be best suitable for the further stage of the research work, consolidated results are given below of the best samples so far.

BET analysis is conducted to quantitatively assess surface morphology, including specific surface area and average pore diameter/size, using a BET-surface area analyzer. Figure 6.8 presents the comparative BET results of non-activated carbon and both activated carbons. PACH activated carbon demonstrates a significant specific surface area of 151.42 m^2/g, notably higher than non-activated carbon PC and PACK, which exhibit values of 2.73 m^2/g and 8.68 m^2/g, respectively. The pore size, ranging 2-10 nm, is highly conducive to ion buffering and can facilitate rapid ion diffusion, thus indicating a high-rate capability for the activated carbon produced. These findings are summarized in table 6.3.

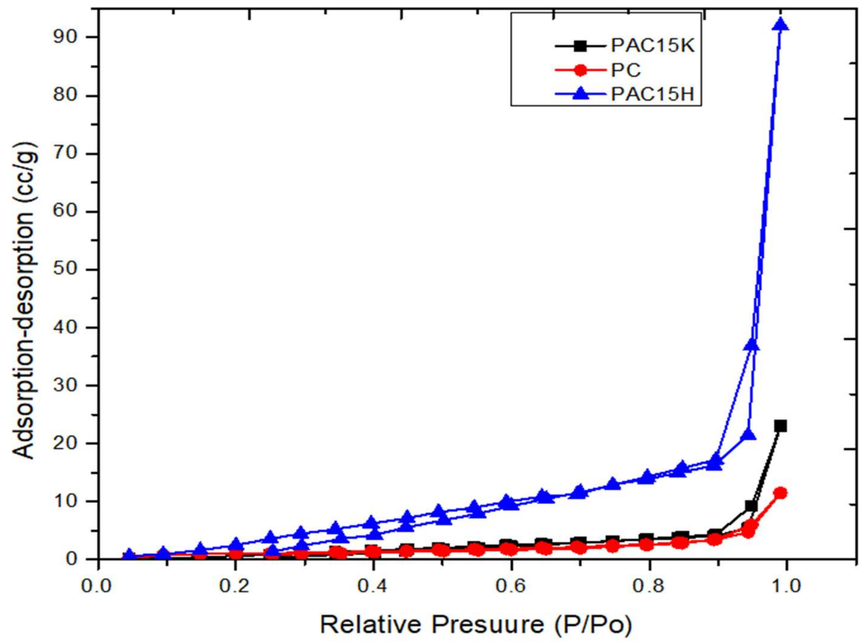


Figure 6.8: Comparative BET graphs of PC, PACK and PACH

Table 6.3: Comparison of major functional carbons synthesized in this work

Sample material (X)	Activation agent (A)	Sample code	Carbon content (%)	Average Pore size (nm)	Specific surface area (m^2/g)
Non-Activated Parali Carbon	-	PC	35.71	3.65	2.73
Parali Activated Carbon	KOH	PACK	49.95	2.65	8.68
	H_3PO_4	**PACH**	**99.85**	**2.72**	**151.42**

6.2.2. Supercapacitor Device Performance Evaluation

Electrochemical double layer capacitance of Parali derived carbon electrodes

Carbonaceous materials, particularly biomass-derived ones, exhibit significant potential for energy storage in supercapacitors, showcasing exponential growth. Supercapacitors operate based on the principle of charge separation at the electrode-electrolyte interface, forming an electrochemical double layer. The performance of a supercapacitor hinges on both the carbon material used for electrode fabrication and the activation method employed.

Initially, activated carbon derived from Parali underwent assessment for specific surface area and subsequent evaluation for suitability in supercapacitor applications. Testing was conducted using a three-electrode configuration with an aqueous 6M KOH electrolyte to analyze charge storage properties. Following are CV profiles of some of electrodes fabricated with different mass loading thus having different current densities which is tabulated later on for calculations.

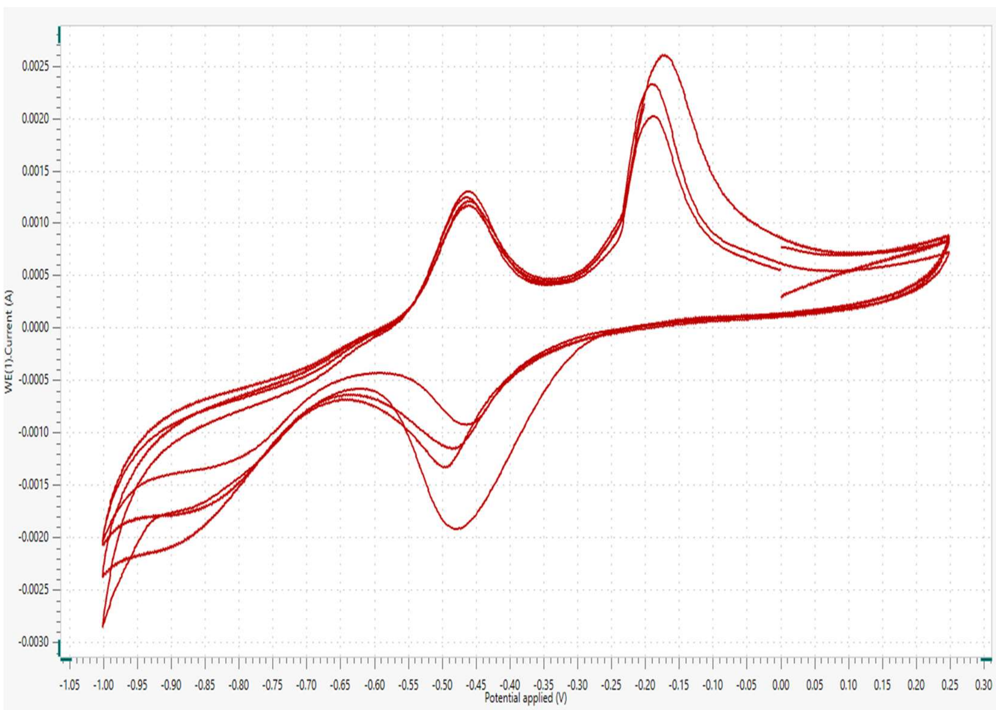


Figure 6.9: CV curve for PC electrode p1

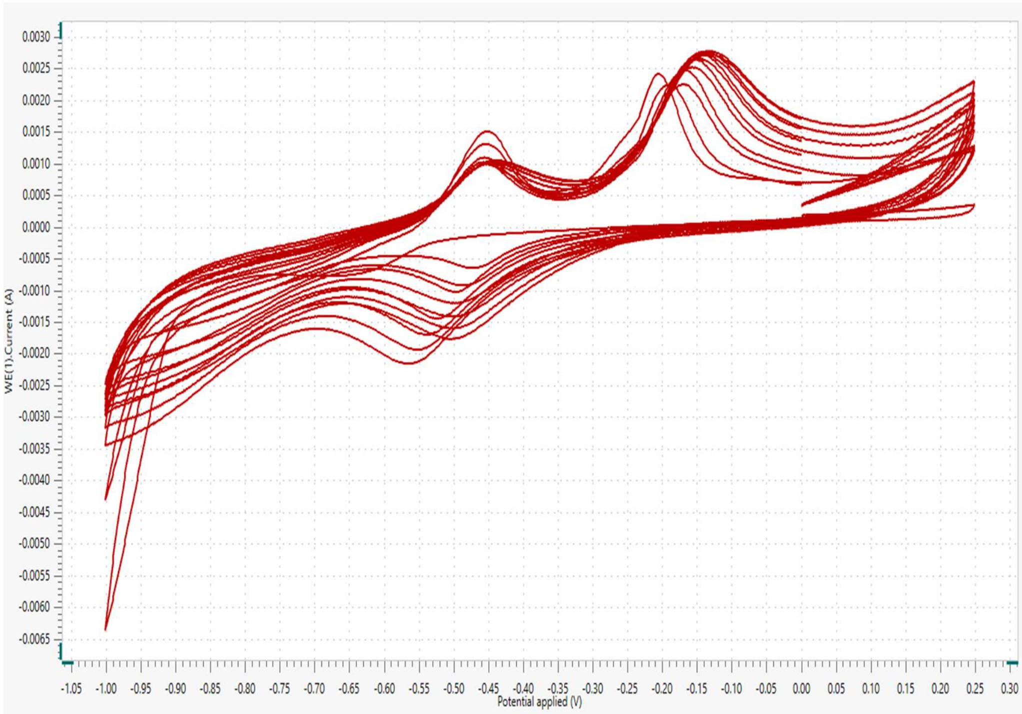


Figure 6.10: CV curve for PC electrode p3

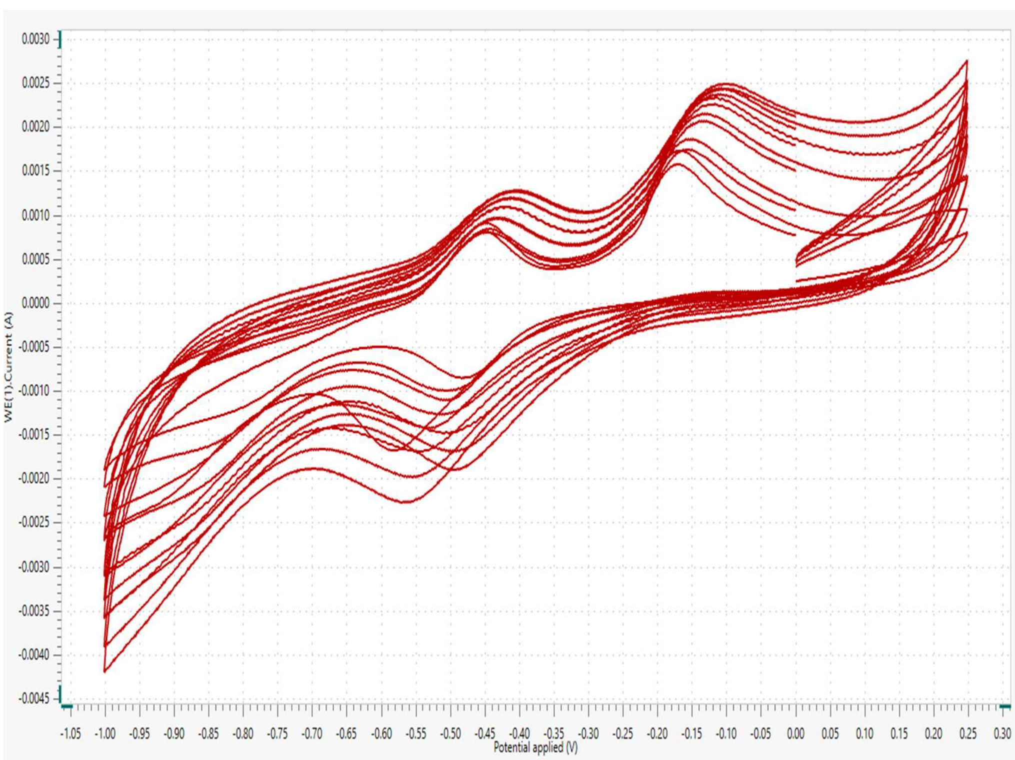


Figure 6.11: CV curve for PC electrode p5

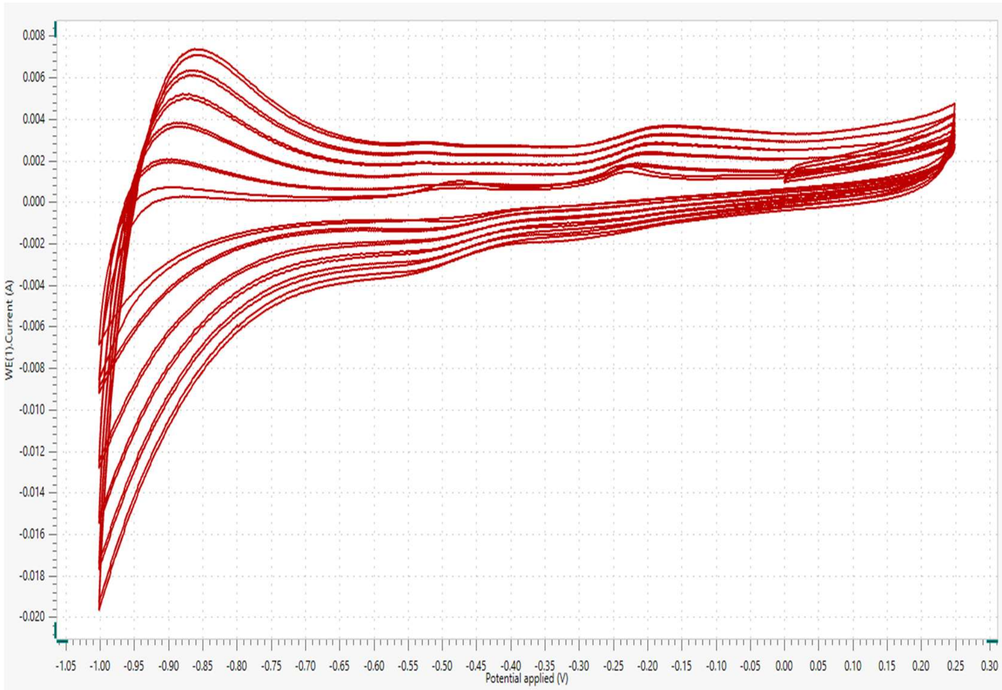


Figure 6.12: CV curve for PACK electrode pk1

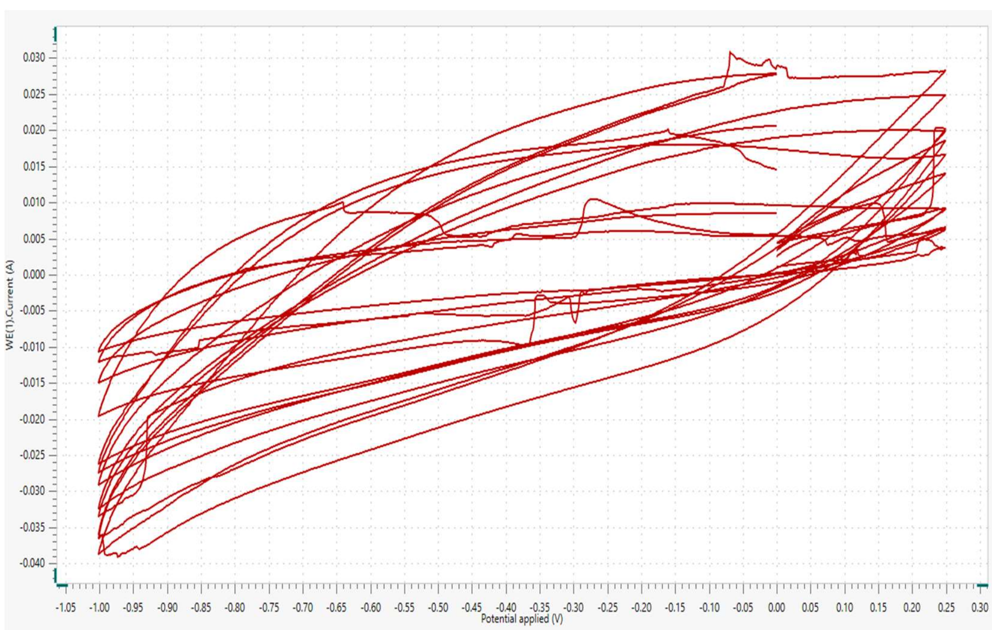


Figure 6.13: CV curve for PACK electrode pk3

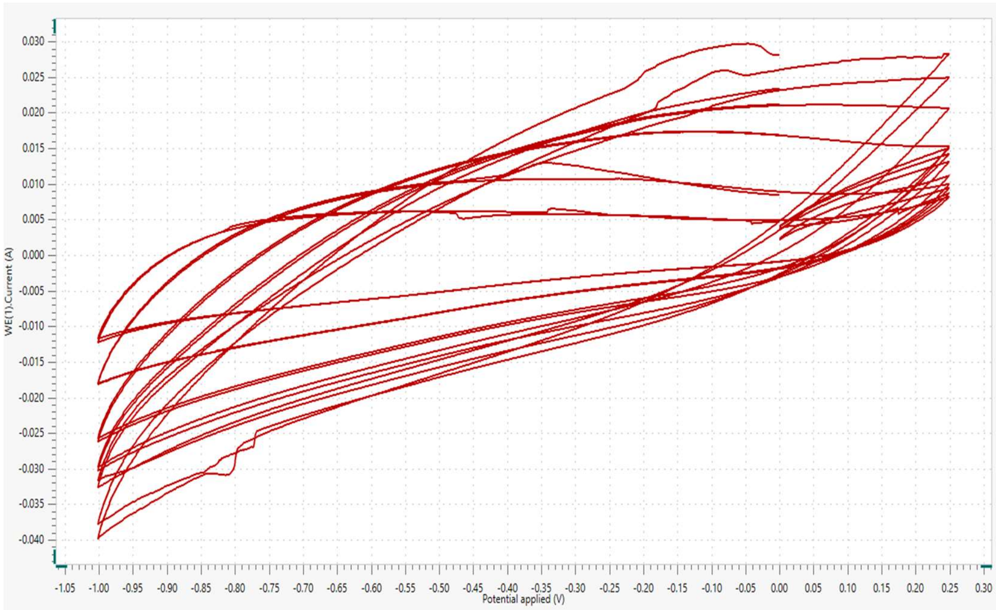


Figure 6.14: CV curve for PACK electrode pk5

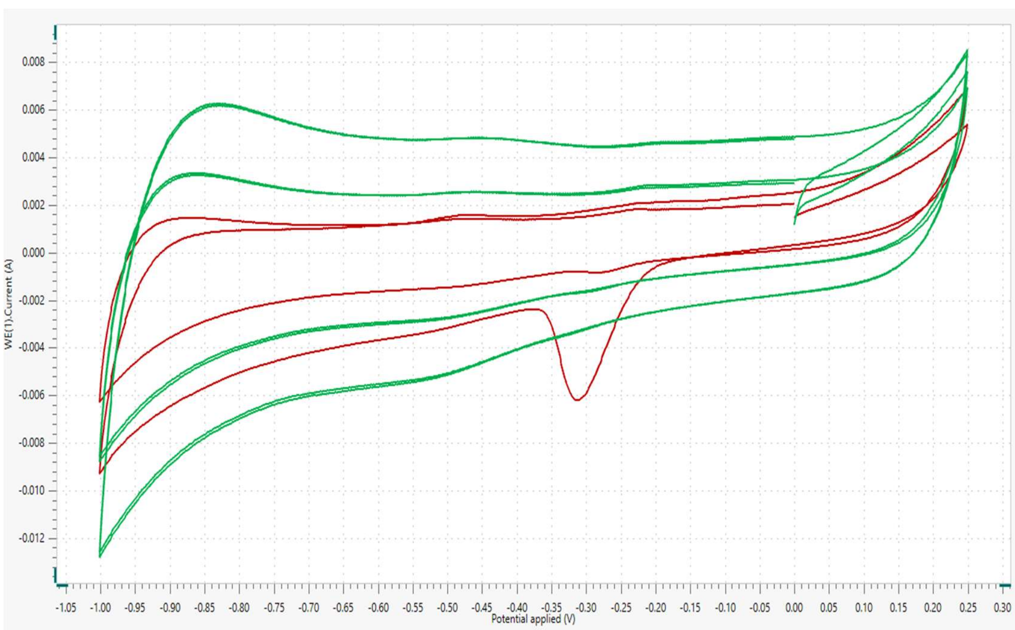


Figure 6.15: CV curve for PACH electrode ph1

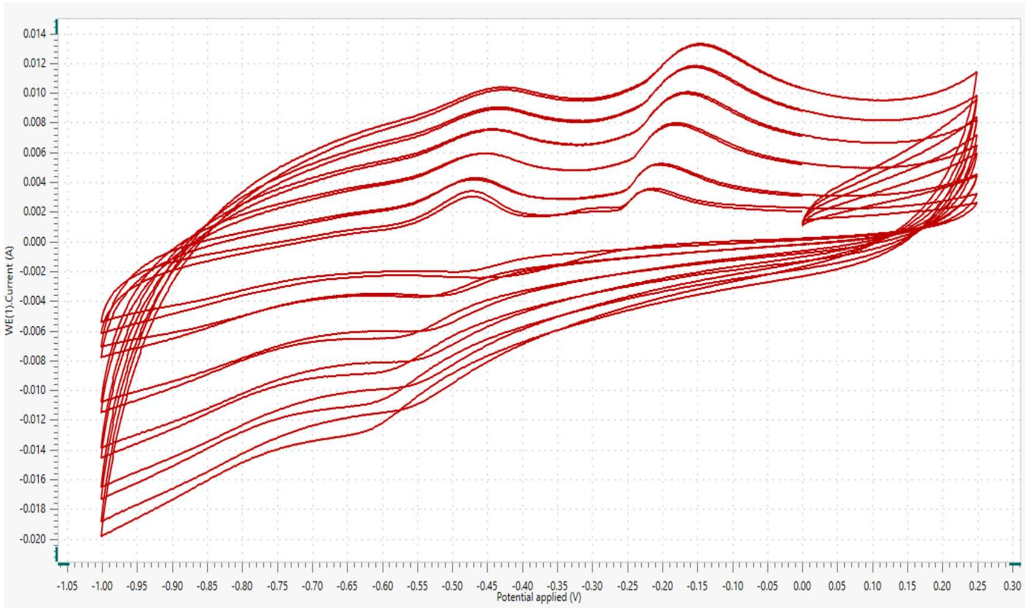


Figure 6.16: CV curve for PACH electrode ph3

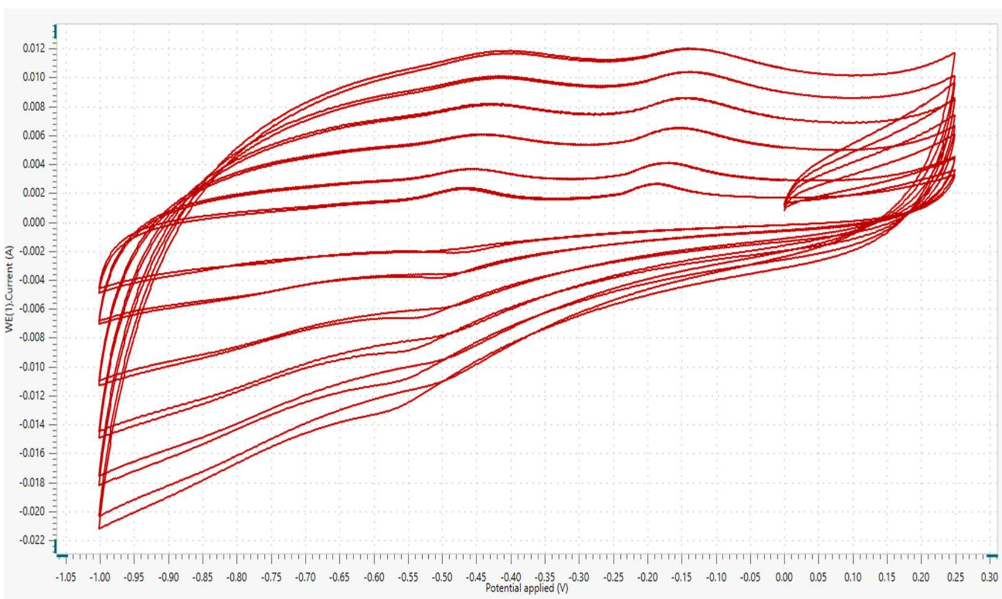


Figure 6.17: CV curve for PACH electrode ph5

Figures 6.9-6.17 depict cyclic voltammetry (CV) curves obtained within the potential range of -1 to 0.25 V vs Ag/AgCl in 6M KOH (i.e voltage window = 1.25 V). These curves correspond to different electrodes fabricated from PC (non-activated), PACK (activated), and PACH (activated) carbons. These curves vary based on active mass loading, current densities, and electrolyte used for analysis. Optimal results indicate charge storage resulting from the formation of the electrochemical double layer at both electrode-electrolyte interfaces. Increasing scan rates of the input voltage lead to heightened currents, signifying excellent rate capability of the prepared electrodes. As scan rates increase, resulting in enhanced current response, slight peaks appear in the CV curves around -0.2 V, attributed to minor pseudo-capacitance, particularly notable in optimal CV performance. It is known that silicon-containing carbon materials exhibit some pseudo-capacitance. Parali, known to contain silicon impurities, can potentially be extracted for reuse in the silicon industry. Minor peaks in the CV curves suggest Faradic reactions at the electrode surface, indicating the presence of OH or NH groups contributing to overall pseudo-capacitance via redox reactions promoted by the lone pair of electrons from these functional groups.

The optimized potential window is documented to be -1 to 0.25 V. CV was not done for all electrodes made as the electrodes that gave bad results on GCD was not tested for CV curves. The potential window is -1 to +0.25 V = 1.25V for all electrodes as can be seen from the CV curves.

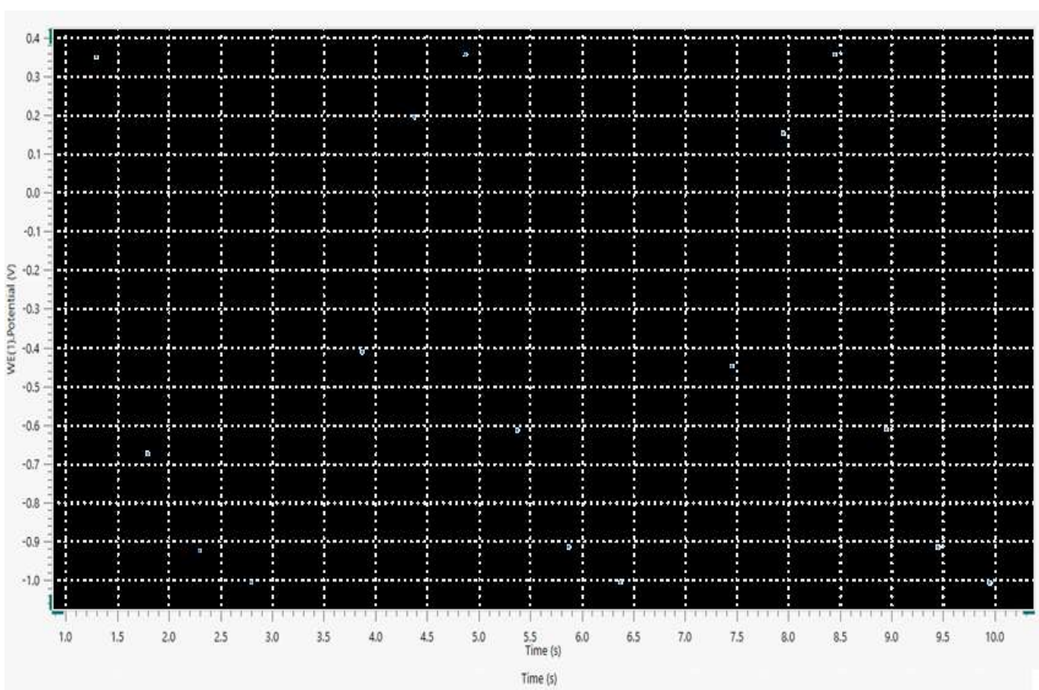


Figure 6.18: GCD of PC electrode p1 (dt = 1s)

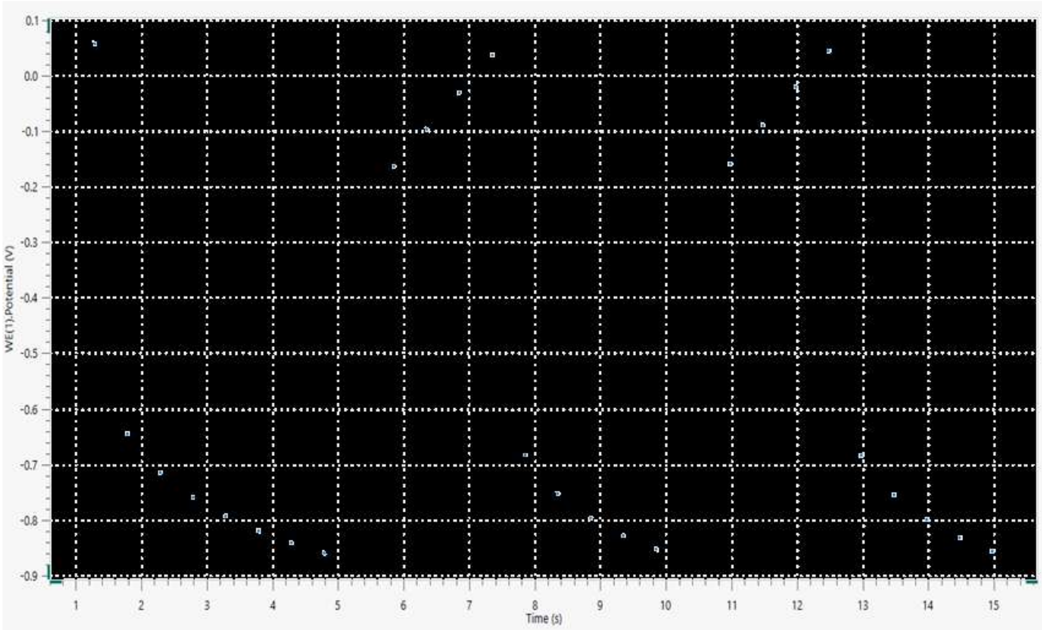


Figure 6.19: GCD of PC electrode p2 (dt = 2.5s)

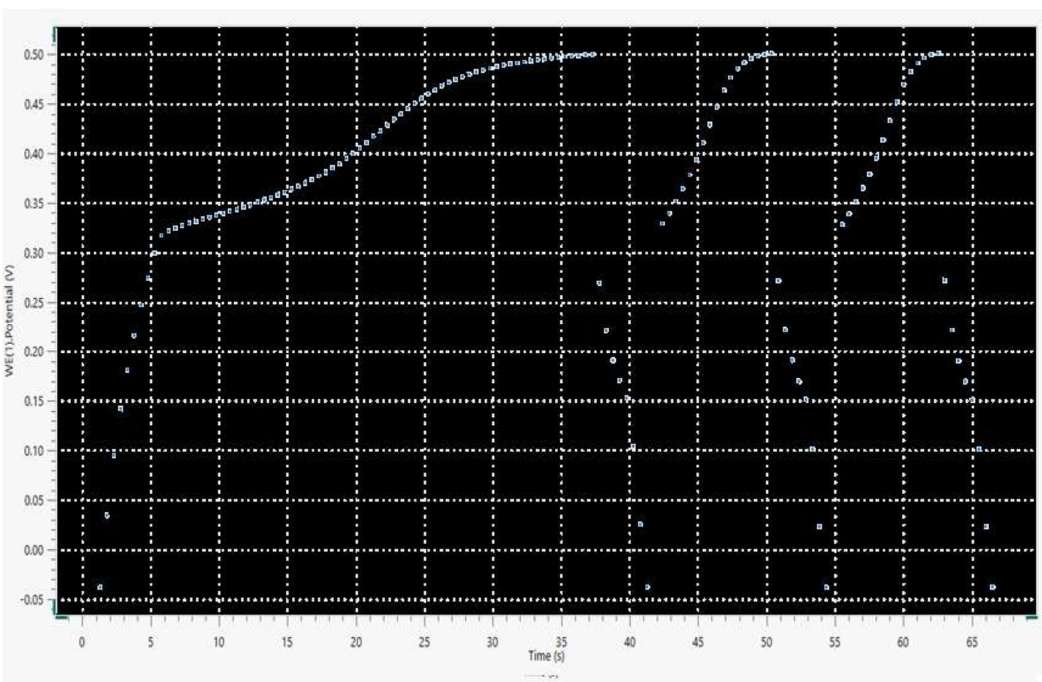


Figure 6.20: GCD of PC electrode p3 (dt = 3.5s)

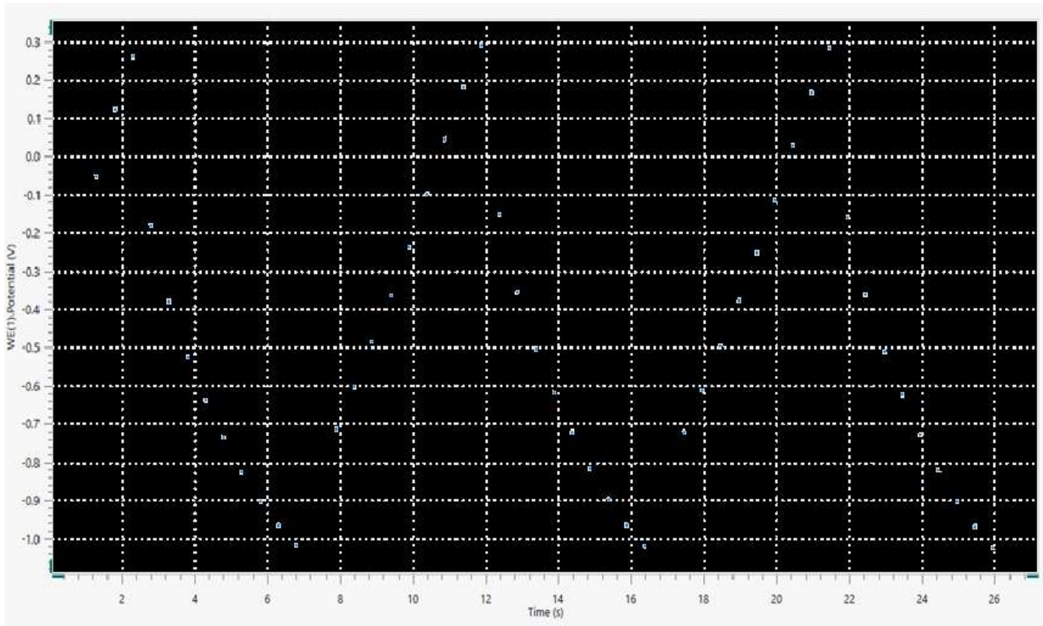


Figure 6.21: GCD of PC electrode p4 (dt = 4s)

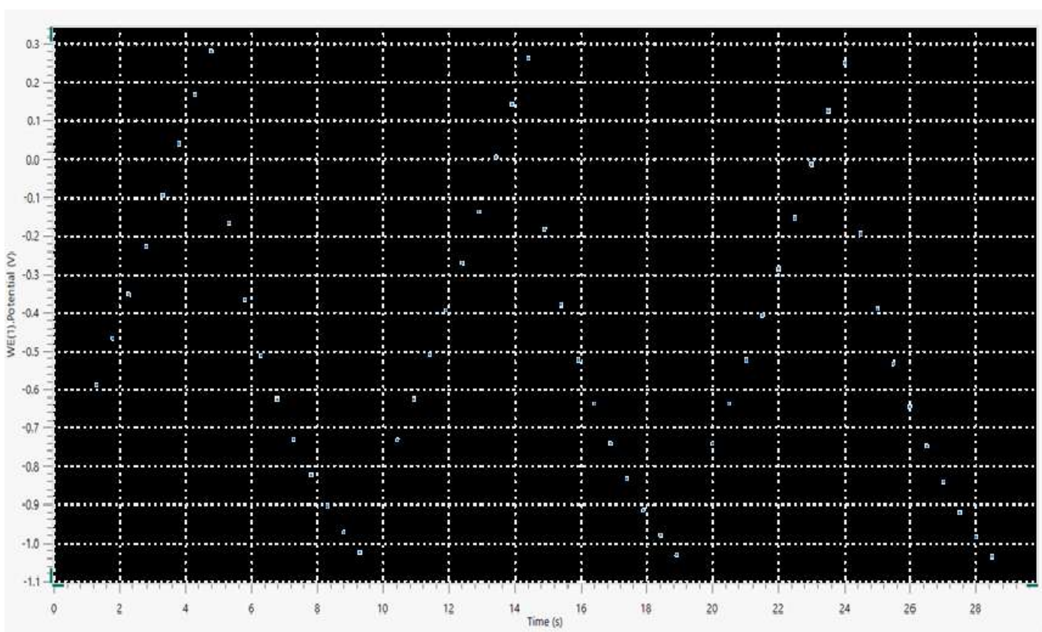


Figure 6.22: GCD of PC electrode p5 (dt = 4.5s)

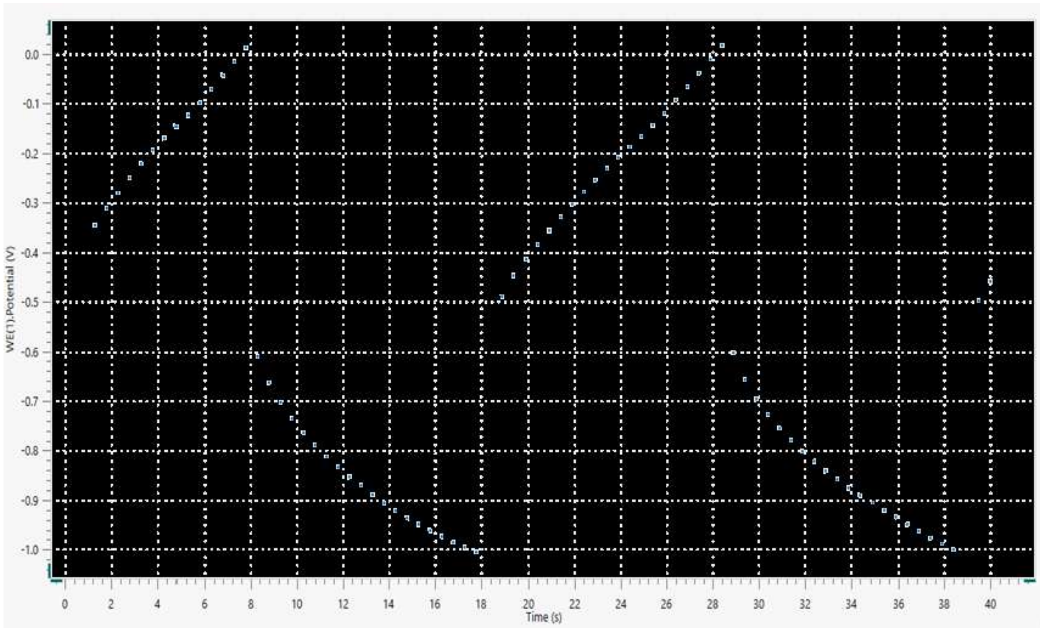


Figure 6.23: GCD of PACK electrode pk1 (dt = 9.5s)

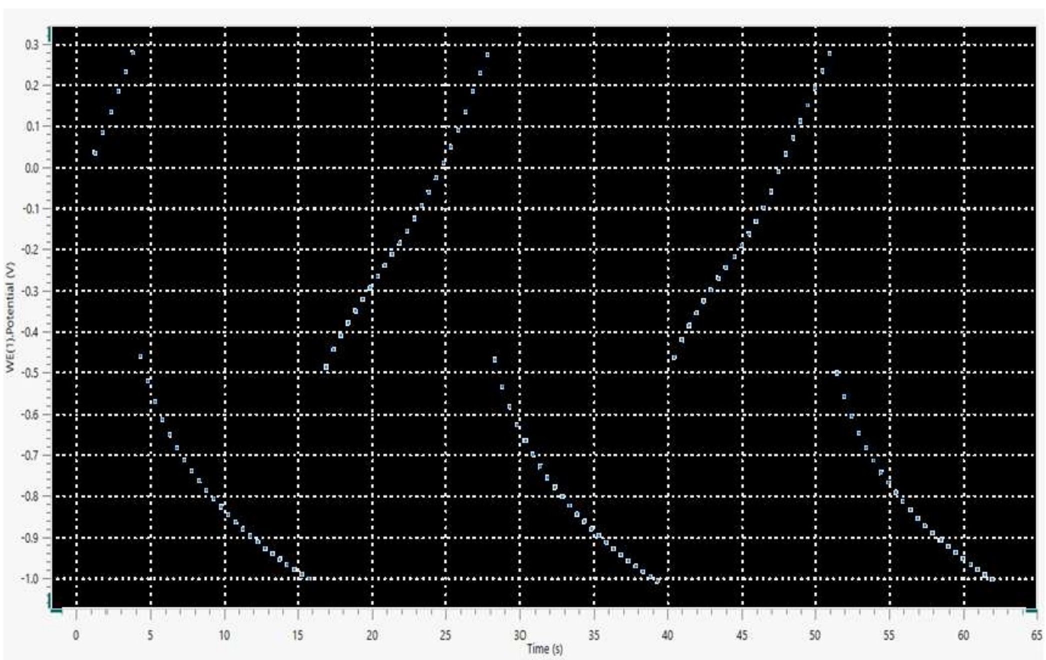


Figure 6.24: GCD of PACK electrode pk2 (dt = 10.5s)

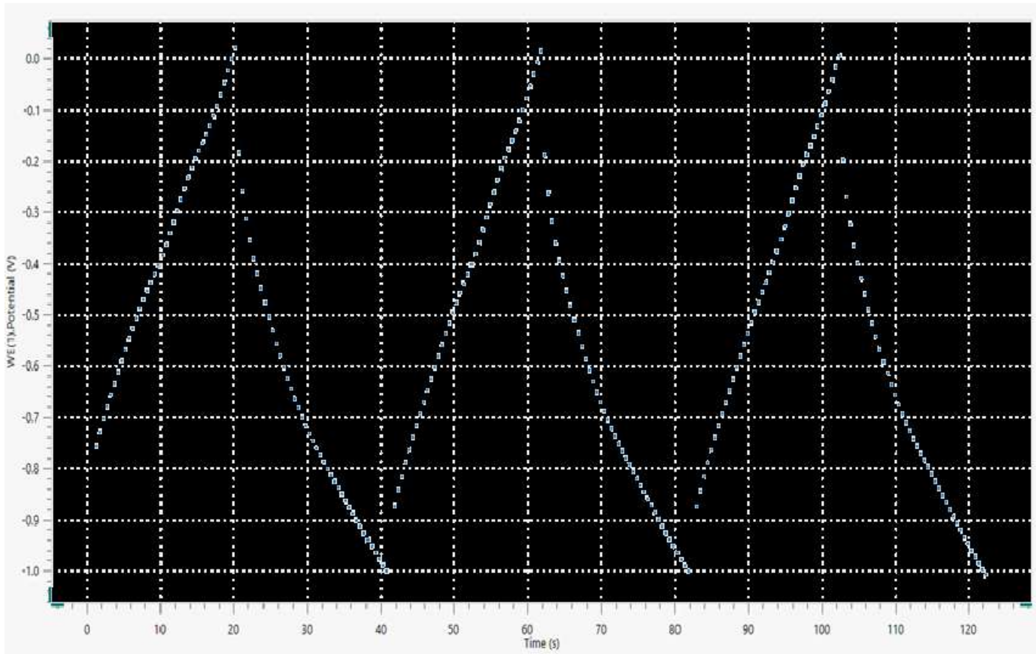


Figure 6.25: GCD of PACK electrode pk3 (dt = 19.5s)

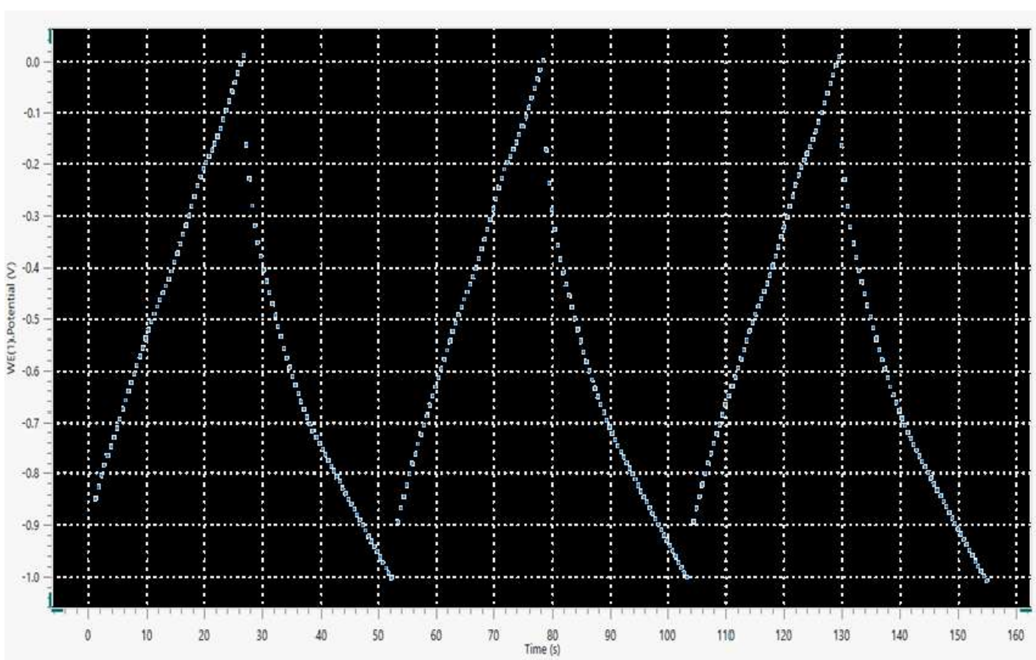


Figure 6.26: GCD of PACK electrode pk4 (dt = 24s)

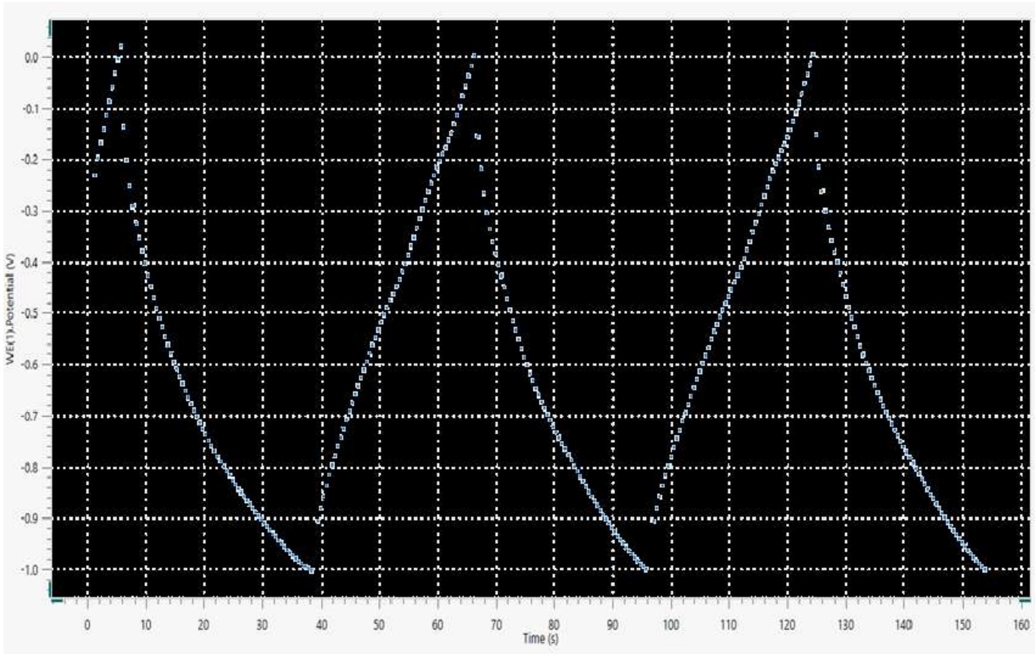


Figure 6.27: GCD of PACK electrode pk5 (dt = 29s)

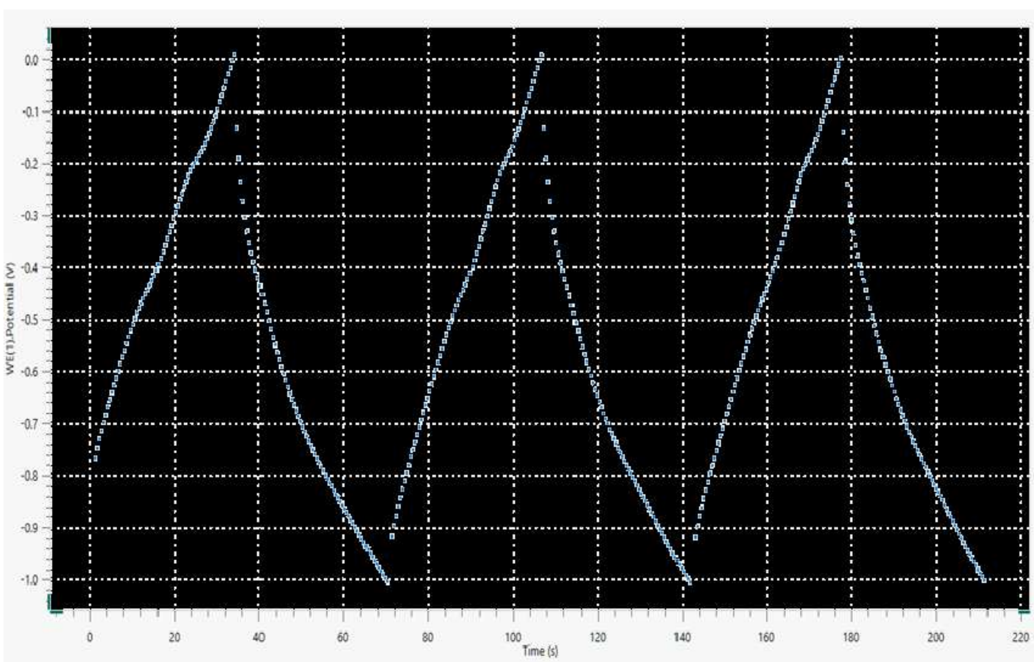


Figure 6.28: GCD of PACH electrode ph1 (dt = 34s)

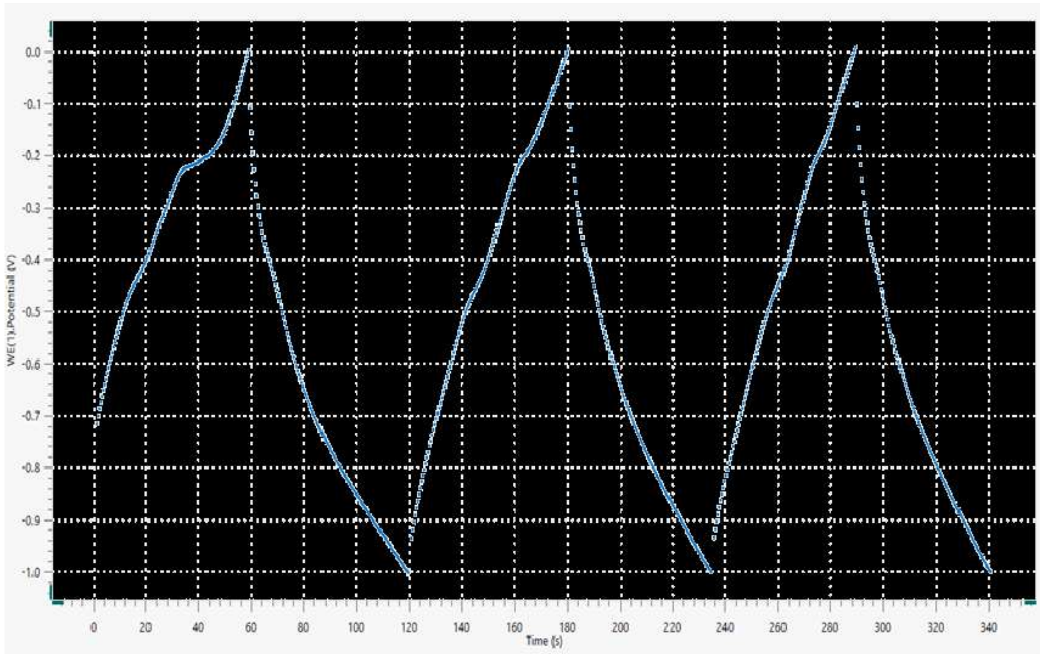


Figure 6.29: GCD of PACH electrode ph2 (dt = 65s)

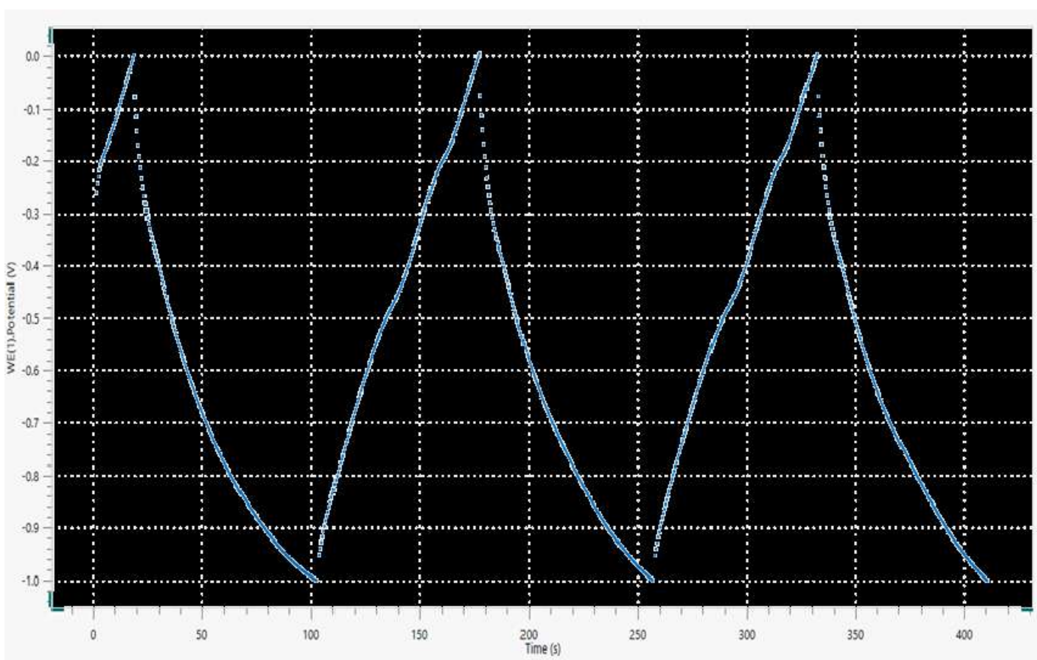


Figure 6.30: GCD of PACH electrode ph3 (dt = 82s)

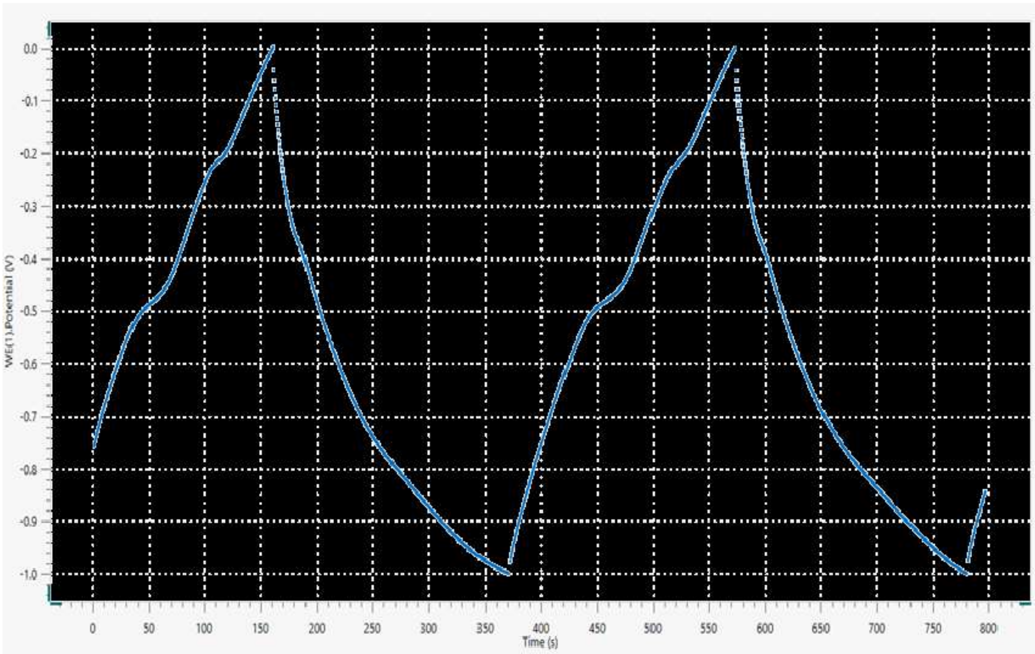


Figure 6.31: GCD of PACH electrode ph4 (dt = 210s)

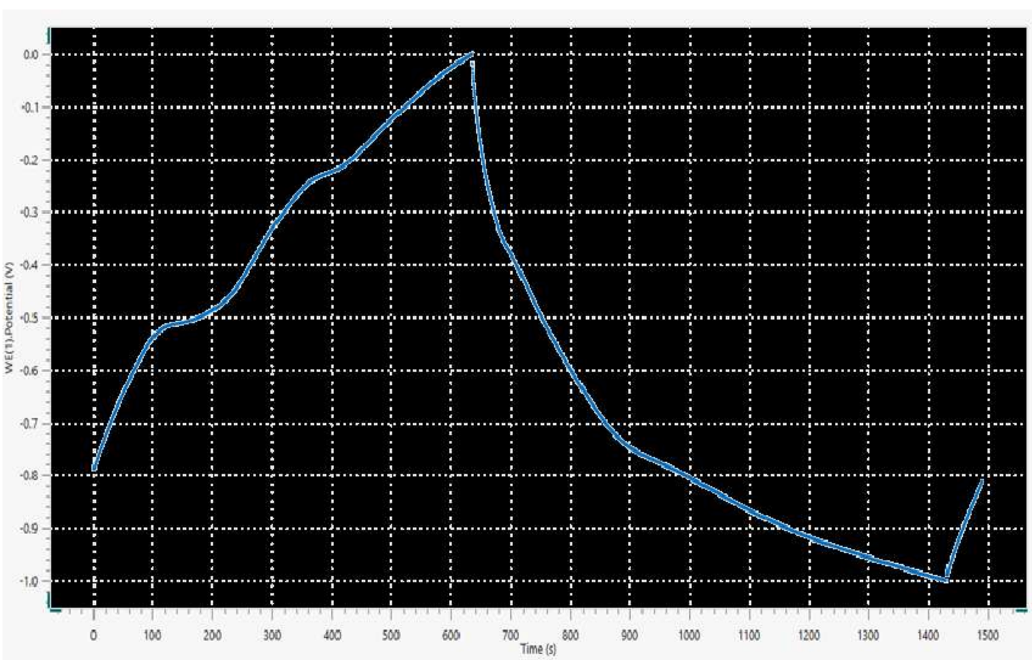


Figure 6.32: GCD of PACH electrode ph5 (dt = 774s)

Table 6.4 shows the EWS results of the various electrodes made from the activated and non-activated carbons prepared during the experimental works out of which one best is directly incorporated in supercapacitor.

The following calculations were incorporated to find the values of specific capacitances at different conditions as well as corresponding energy densities[126]:-

For Specific capacitance (**C**):

C = Current density * time / voltage …………………………..(1)

For Ph5 electrode of PACH, C = 0.4 x 774 /1.25 = **247.68 F/g**

Similarly, all the specific capacitances have been calculated using equations given above[126] and tabulated in table 6.4.

Now for **Energy density** is given by[126]

E = 1/7.2 * CV² ……………………………………………………..(2)

The energy densities with respect to the specific capacitance values were also calculated using the equation 3[126] and are tabulated in table 6.4.

The maximum energy density achieved in this work is **54 Wh/Kg** as shown in table 6.4.

Material used	**Electrode *(see GCD profiles)***	**Time (dt) in sec.**	**Current density (J) in A/g**	**Specific capacitance (C) = J *dt/V in F/g (V = 1.25)**	**Energy density (E) = $CV^2/7.2$**
PC	P5	4.5	0.4	1.44	0.31
	P4	4	0.8	2.56	0.55
	P3	3.5	1.2	3.36	0.73
	P2	2.5	1.6	3.20	0.35
	P1	1	2.0	1.60	0.34
PACK	Pk5	29	0.4	9.28	2.01
	Pk4	24	0.8	15.36	3.34
	Pk3	19.5	1.2	18.72	4.06
	Pk2	10.5	1.6	13.44	2.91
	Pk1	9.5	2.0	15.20	3.29
PACH	**Ph5**	**774 (= 12.9 minutes)**	**0.4 (load of LED etc.)**	**247.68**	**54**
	Ph4	210	0.8	134.4	29.16
	Ph3	82	1.2	78.72	17.08
	Ph2	65	1.6	83.20	18.05
	Ph1	34	2.0	54.40	11.80

Table 6.4: Supercapacitor performance comparison for different electrodes

Galvanometric charge-discharge (GDC) studies were conducted to explore the charge storage characteristics of the carbon electrode. It's worth noting that the carbon-based electrodes derived from biomass are designated as negative electrodes.

The symmetric supercapacitor device, designed as a laboratory prototype, utilizes two identical carbon electrodes fabricated from the most optimized carbon material in a 6M KOH aqueous electrolyte. The most optimized sample, PACH, is selected, and the electrode (ph5) derived from it is employed to construct the supercapacitor device. The device is then analyzed under various conditions to assess its supercapacitance properties and determine specific capacitance and energy density, aligning with the objectives of the study.

Figure 6.33 illustrates the cyclic voltammetry (CV) curves obtained within the potential window of -1 to 0.25 V vs Ag/AgCl in 6M KOH at different scan rates for the final supercapacitor device. These curves exhibit a distinctly rectangular shape, indicating that the charge-discharge process occurs via the phenomenon of electrical double layer formation. The observation of increasing current with higher scan rates further confirms the high-rate capability of the device.

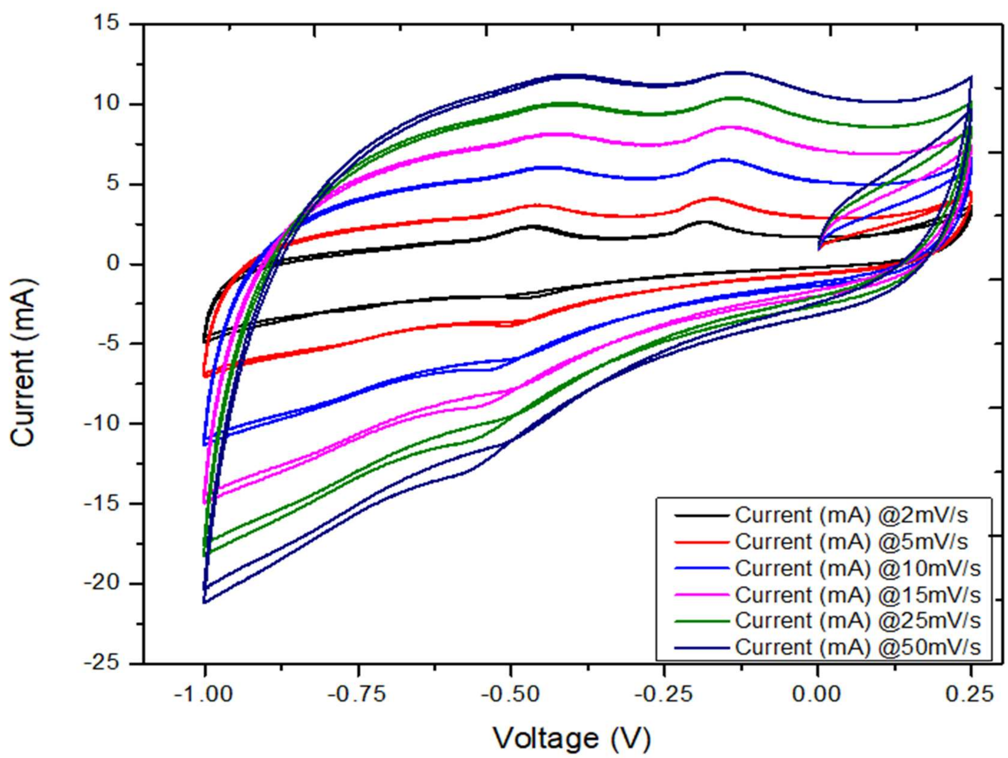


Figure 6.33: CV curves of the Supercapacitor device recorded at different scan rates

The below figure 6.34 presents the specific capacitance as a function of scan rate.

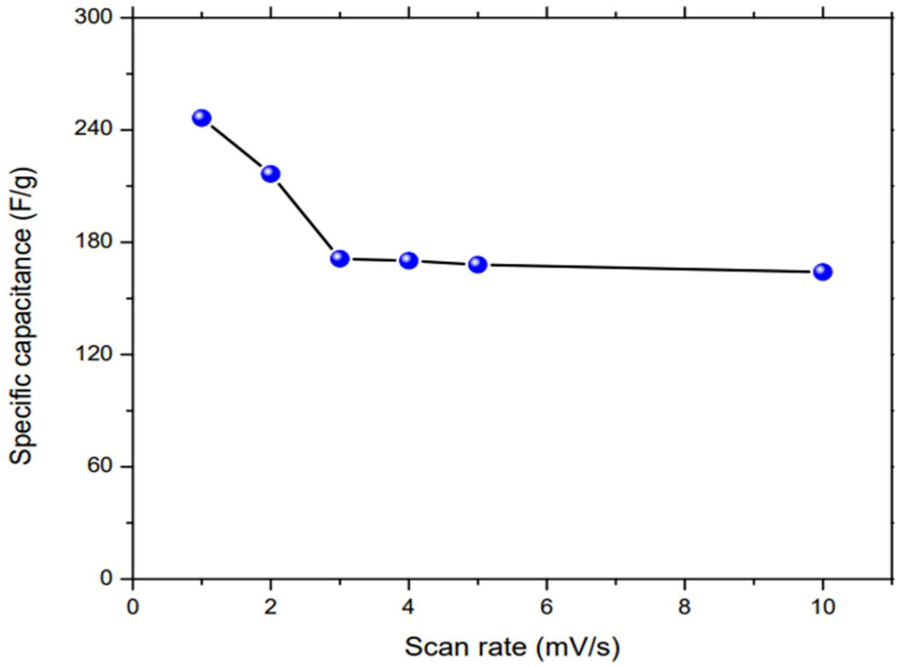


Figure 6.34: Specific capacitance as a function of scan rate

Additionally, as shown below, figure 6.35 showcases the charge-discharge curves (GCD profiles) for the device (made from the electrode ph5), which demonstrate remarkable symmetry at each current density. This symmetry suggests excellent reversible charge storage with very high coulombic efficiency.

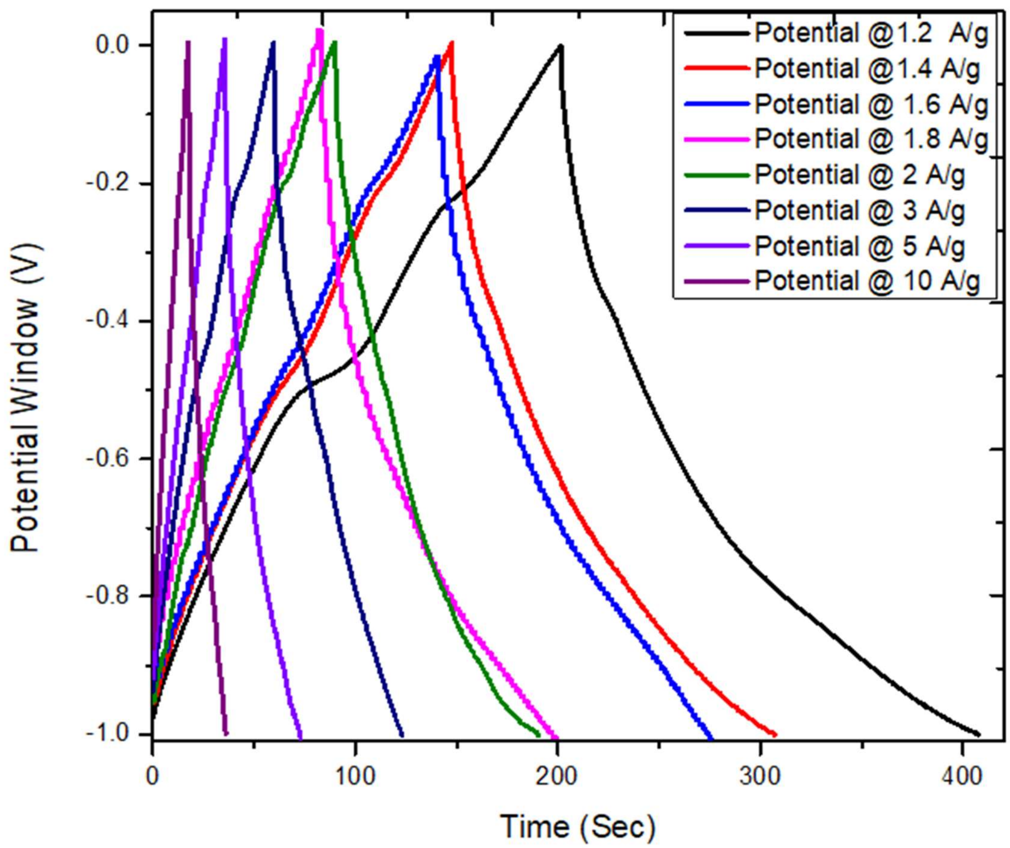


Figure 6.35: GCD profiles of Supercapacitor device at various current densities

The below figure 6.36 illustrates the specific capacitance as a function of current density for the device. At low current densities, more surface area is effectively utilized, resulting in higher specific capacitance. However, at higher current densities, fast charging and discharging occur, leading to less surface area utilization and consequently lower specific capacitance. It is observed that the device exhibits a maximum specific capacitance of 247.6 F/g and a stable specific capacitance of 180 F/g at a high current-densities as can be seen from figure 6.36. Specific capacitance for hard carbon biomass material typically ranges from 100 to 400 F/g, as reported in various literatures[126, 54].

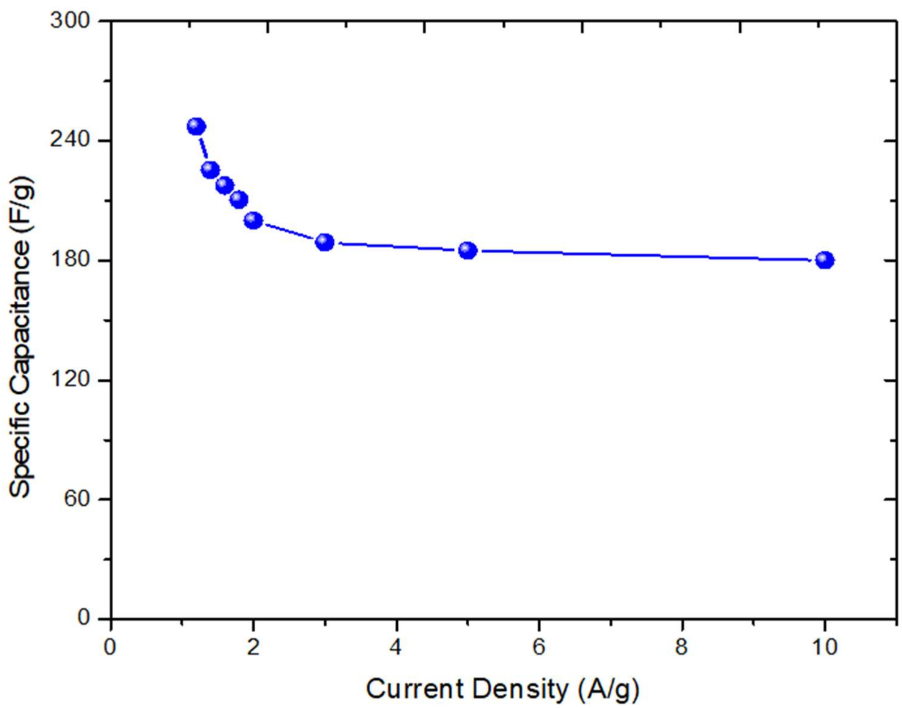


Figure 6.36: Specific capacitance vs current density of the device

The present study demonstrates that the supercapacitor device constructed from Parali-derived activated carbon electrodes exhibits good specific capacitance due to its crystalline structure, high porosity, substantial surface area, and high carbon content achieved through the employed functional carbon synthesis methodology. The porous carbon network facilitates multidimensional ion/electron transport with easy access to the electrolyte, resulting in excellent charge storage[126].

The energy and power density are calculated using a methodology presented in[126]. The relationship between energy density and power density is depicted in below figure 6.37, commonly referred to as a 'Ragone plot'. The maximum energy density achieved was 54 Wh/kg at a power density of 243 W/kg, while at even higher power density of 4000 W/kg, an energy density of 10 Wh/kg was maintained.

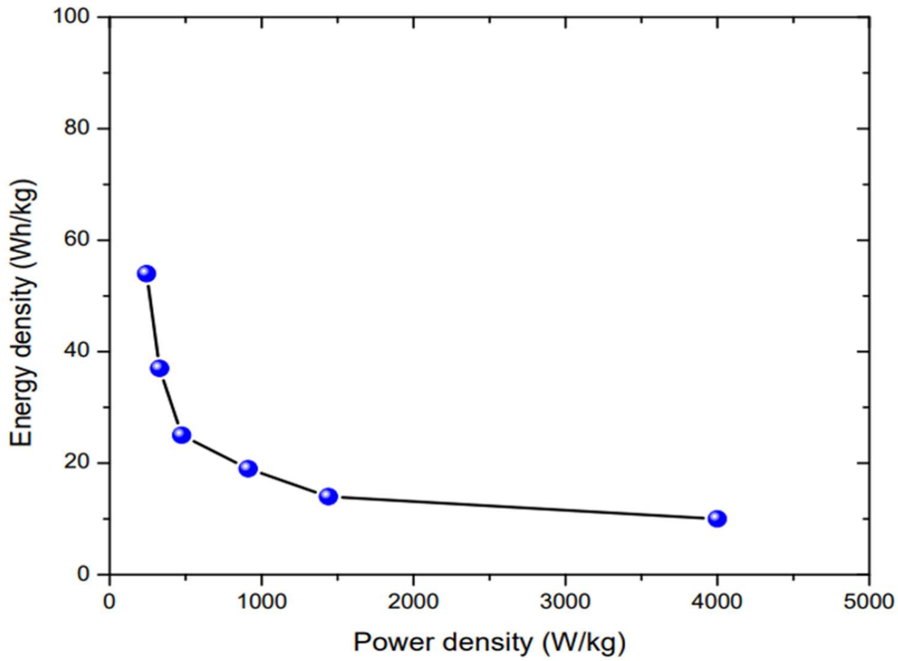


Figure 6.37: “Ragone plot showing energy density variation with power density”

Cycle ability and efficiency testing for the “symmetric supercapacitor device” in aqueous electrolyte were conducted over 5000 cycles, with results presented in below figure 6.38. The high Coulombic efficiency, evidenced by similar charging and discharging profiles for the first three and last three cycles, approaches nearly 100% over long cycles. This observation suggests that the prototype supercapacitor device exhibits high stability and robustness.

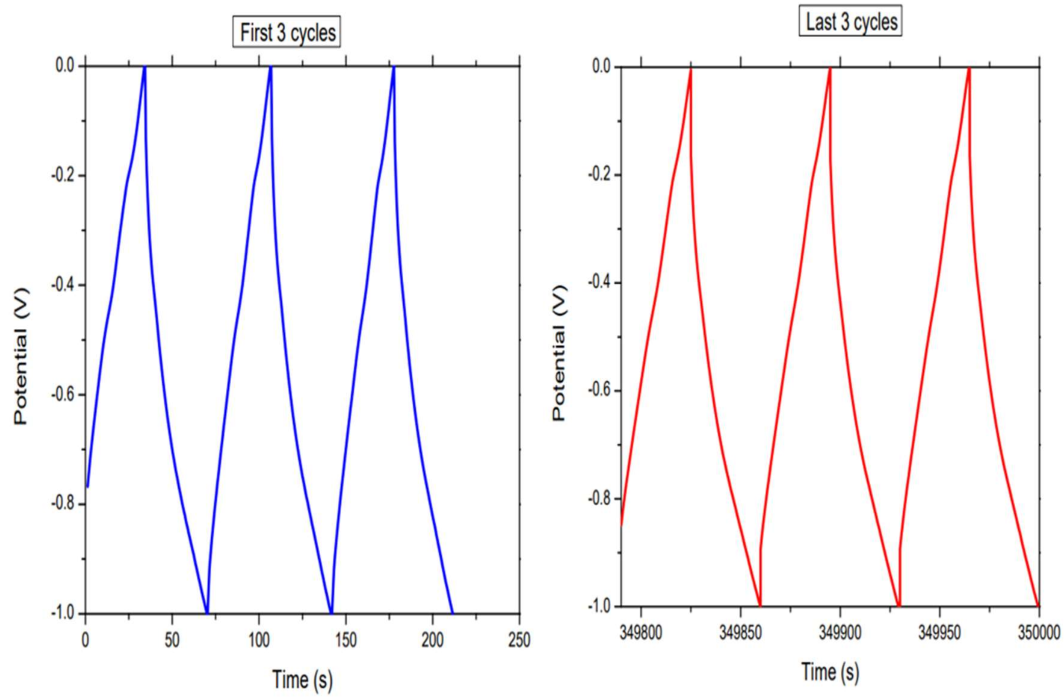


Figure 6.38: Showing test cycles for first and last three cycles (5000 cycles) of performance of the device.

The variation in Coulombic efficiency with respect to the number of cycles is illustrated in below figure 6.39.

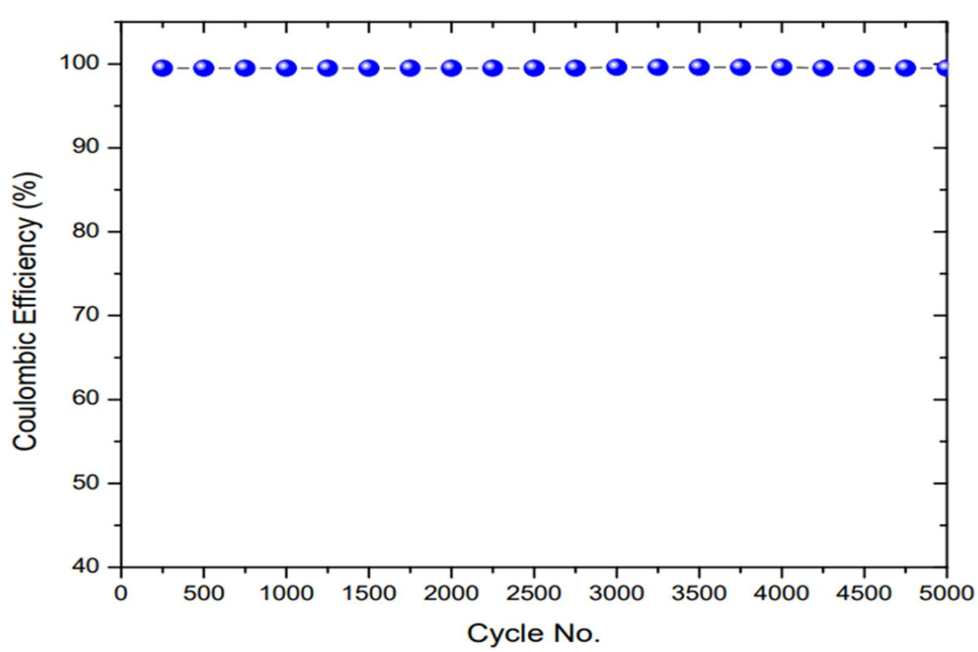


Figure 6.39: Coulombic Efficiency vs Cycle no.

In assessing the reliability and reproducibility of the fabricated supercapacitor, figures 6.38 and 6.39 serve as key indicators. Long-term stability is crucial for practical supercapacitor applications, thus cycling stability of the “Symmetric device in aqueous electrolyte” was evaluated over an extended duration. The observed high Coulombic efficiency throughout the lengthy cycles underscores the robustness and stability of the prototype device. Notably, “the consistent charging and discharging times recorded during the initial three cycles and the last three cycles”, which are nearly identical, affirm nearly 100% Coulombic efficiency. Consequently, the fabricated device exhibits high reliability, stability, and reproducibility.

Figure 6.40: Supercapacitor device proto-type (Device 1) running a dc motor and an LED bulb successfully

Thus, it can be concluded that the laboratory prototype supercapacitor device, comprising Parali biomass-derived carbon electrodes, demonstrates commendable supercapacitance characteristics in terms of charging and discharging, stability, and notable power and energy density. To further substantiate this claim, the laboratory prototype supercapacitor device was tested for practical applicability in powering two consumer electronics: an LED bulb and a DC motor, as depicted in figure 6.40. After a full charge, the device could operate a “DC motor for 12.5 minutes” and an “LED bulb for 14 minutes”.

Notably, the LED bulb operated for a slightly longer duration compared to the DC motor, likely due to mechanical and thermal losses inherent to the DC motor. In conclusion, the device demonstrates the capability to power such devices for a significant duration on a single charge, as demonstrated by figure 6.40, showcasing the real-time operation of the prototype device successfully driving both a DC motor and an LED bulb respectively.

Table 6.5 provides a comparison of the energy density of supercapacitors reported in various previous literature sources with the value obtained in the present study. It is evident that both the energy density and power density results significantly surpass those reported in previous literatures.

Specifically, the energy density achieved in the current work surpasses those reported for biomass-derived devices in prior studies. For instance, in a study cited as[116], bagasse was utilized, resulting in an energy density of 20 Wh/kg. In another study, catkins biomass was employed, yielding an energy density of 37.9 Wh/kg in 6M KOH aqueous electrolyte[129].

Table 6.5: Comparative results of Parali Supercapacitor

S. No.	Biomass material used	Electrolyte used	Final Device Energy density (Wh/Kg)	Literatures
1	Waste coffee beans	1M H_2SO_4	10	[130]
2	Bagasse	1M Na_2SO_4	20	[116]
3	Left over rice	1M $TEABF_4$	22.6	[132]
4	Quinoa	6M KOH	9.5	[87]
5	Bean dregs	1M Na_2SO_4	25.9	[89]
6	Bamboo	3M KOH	10.9	[134]
7	Silkworm	PVA/H_2SO_4	19.6	[135]
8	Pumpkin	1M Na_2SO_4	22.1	[136]
9	Catkins	6M KOH	37.9	[129]
10	**Parali**	**6M KOH**	**54**	Proposed work

6.3. Thermal Energy Storage (TES): PCM Heat Exchanger (Device 2)

6.3.1. Material Characterization

6.3.1.1 Thermo physical studies of PEG-4000:

The stability of the phase change material (PCM) utilized in the latent heat storage system is crucial, particularly after undergoing numerous charging and discharging cycles. Accelerated thermal cycling was employed to assess the thermo-physical properties of PEG-4000. The melting temperature and latent heat of fusion were measured over one thousand thermal cycles at intervals of 100 cycles. Notably, PEG-4000-PCM transitions from a solid phase to a liquid phase within a duration of 10 minutes, while the reverse transition from liquid to solid occurs within 15 minutes. The complete cycle of melting and freezing for PEG-4000 takes approximately 25 minutes, as depicted in figure 6.41.

Table 6.6: Thermo-physical properties of PCM PEG-4000

S. No	Property	Range
1	Melting point	58–60 ^oC
2	Density at 60 ^oC	1.092 g/cm^3
3	Latent heat of fusion	150.8 J/g
4	Heat Capacity	171.1 J/g
5	Average molecular weight	3600 - 4000 g/mol

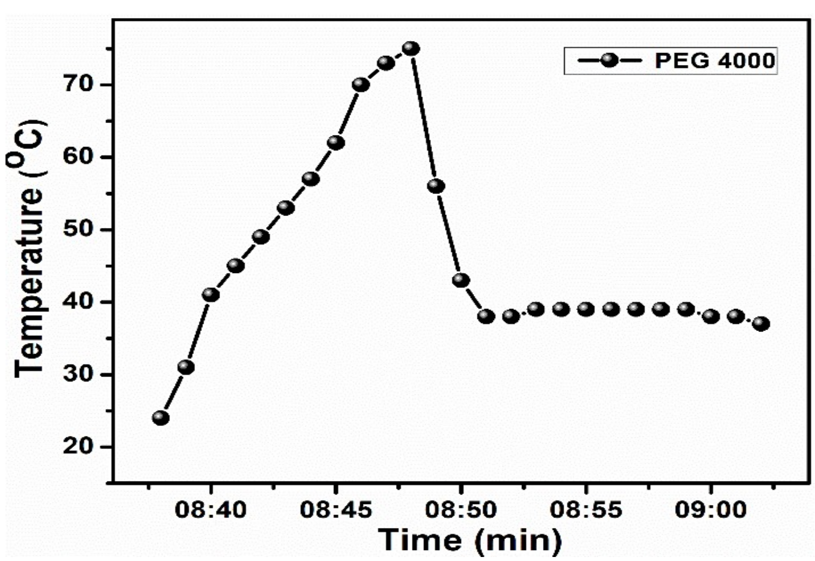


Figure 6.41: Charging and discharging time per cycle of PEG-4000

6.3.1.2 DSC analysis:

Accelerated thermal cycling was executed over 1000 cycles, with measurements of the thermo-physical properties of PEG 4000 taken at every 100 cycles. The differential scanning calorimetry (DSC) curve of PEG-4000 for the 0th, 500th, and 1000th cycles are depicted in below figure 6.42, illustrating variations in the endothermic heat flow rate corresponding to temperature changes.

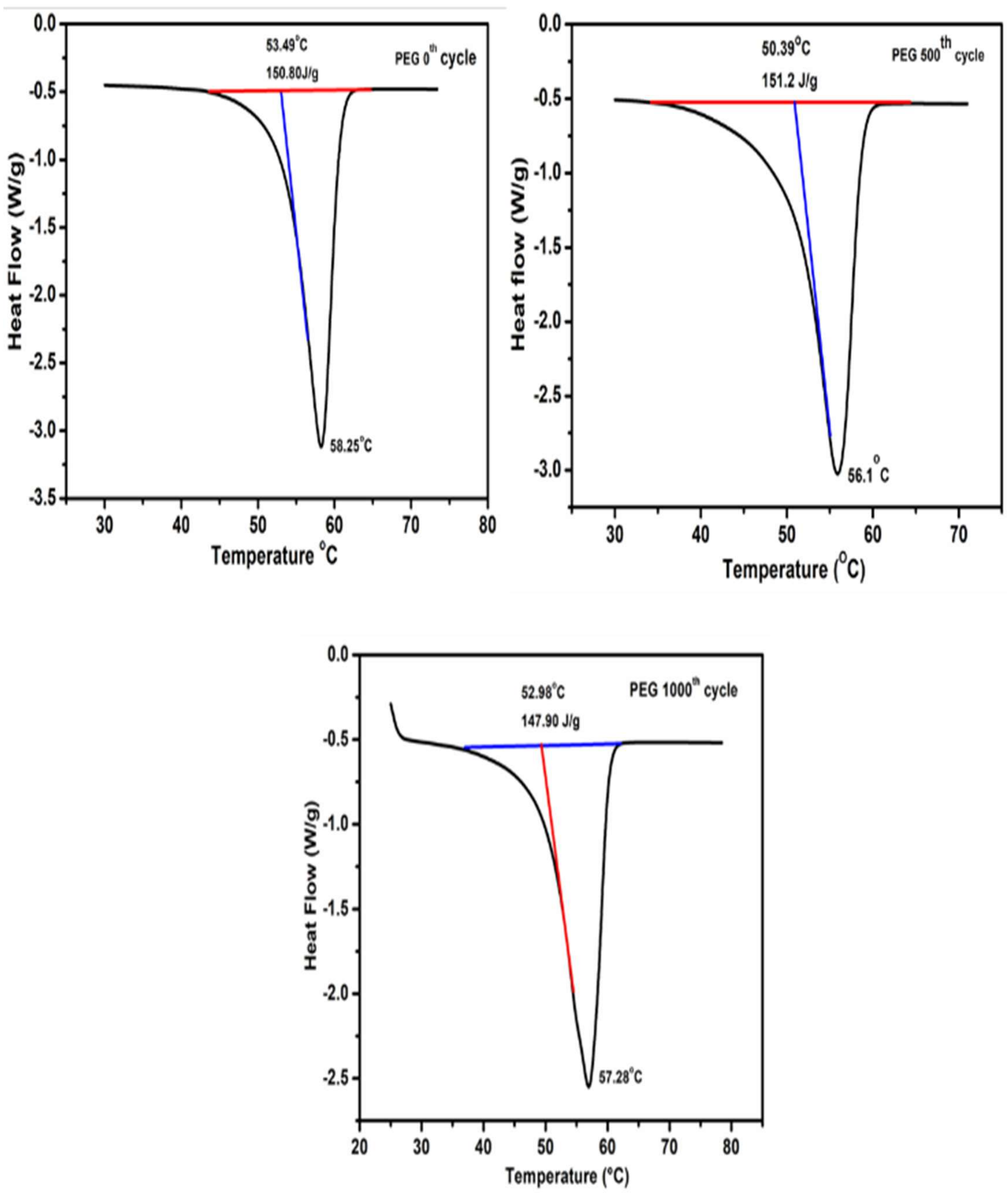


Figure 6.42: DSC curve for 0^{th}, 500^{th} and 1000^{th} cycle of PEG-4000.

6.3.1.3 RPD of LHF and Melting temp. analysis:

The Relative Percentage Difference (RPD) is used to quantify the degree of deviation in the phase transition temperature and latent heat of fusion (LHF) of PEG 4000. The un-cycled PEG-4000 PCM serves as the reference point for comparison. The following formula is used for the calculations [83]:

$$RPD\% = \frac{X_{n,i} - X_{0,i}}{X_{0,i}} \times 100\% \text{ ----------> } (1)$$

X_0,i and Xn,i represent the values of parameter i at the 0th and nth thermal cycle, respectively, where i denotes the latent heat of fusion (LHF) and melting temperature of PEG-4000.

For stability analysis of Latent heat of Fusion (LHF)

Take example of case 500th cycle (Figure 6.42).

RPD for LHF = ((151.20 – 150.80)/150.80) x 100%

= 0.26 %

For stability analysis of Melting or Phase transition temperature (PTT)

Take example of case 500th cycle (Figure 42).

RPD for PTT = ((58.25 – 56.10)/58.25) x100%

= - 3.69 %

Table 6.7: RPD (Relative percentage difference) in Latent Heat of Fusion and Melting temp. of PEG-4000

No. of cycles	Melting Temperature °C	RPD of MT or PTT (%)	LHF J/g	RPD of LHF (%)
0	53.49 - 58.25	-	150.80	-
100	53.99 - 57.70	-0.94	149.70	-0.72
200	55.61 - 59.80	2.66	147.60	-2.12
300	56.94 - 59.93	2.88	150.10	-0.46
400	54.80 - 58.10	-0.25	149.40	-0.92
500	**50.39 - 56.10**	**-3.69**	**151.20**	**0.26**
600	50.40 - 54.90	-5.75	149.10	-1.12
700	50.41 - 57.96	-0.49	148.81	-1.31
800	52.78 - 57.71	-0.92	149.01	-1.18
900	50.46 - 57.00	-2.14	148.90	-1.25
1000	52.98 - 57.28	-1.66	147.90	-1.92

The LHF and melting temperature of PEG 4000, along with their respective RPD% values, are listed in table 6.7. The RPD of the phase transition temperature at the 100th, 500th, and 1000th cycle relative to the 0th cycle is -0.94%, -3.69%, and -1.66%, respectively. The change in LHF for every 100 cycles is depicted in Figure 6.43. Similarly, the RPD of the latent heat of fusion at the 100th, 500th, and 1000th cycles relative to the 0th cycle is -0.72%, 0.26%, and -1.92%, respectively. Following one thousand thermal cycles, the maximum and minimum variations in the melting temperature are 2.88% and -0.25%, respectively, while for LHF, the maximum and minimum variations are 0.26% and -0.46%, respectively. These minimal variations in the properties of PEG-4000 ensure its thermal reliability, rendering it suitable for thermal energy storage applications.

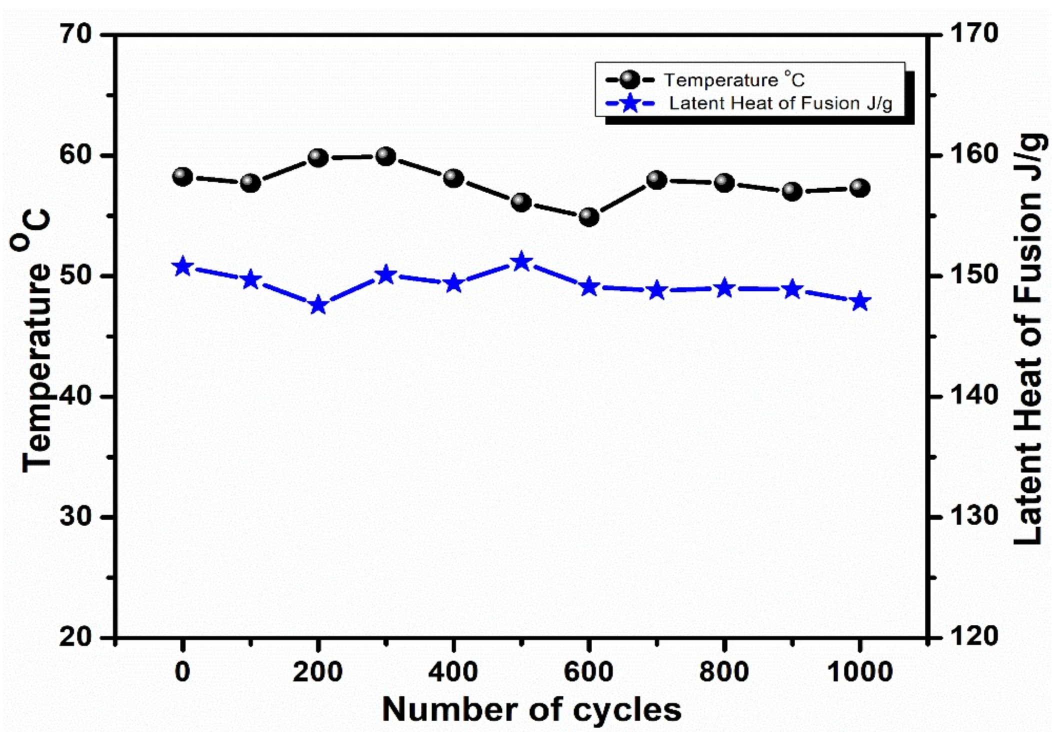


Figure 6.43: Change in LHF and phase transition temperature of PEG 4000 for various thermal cycles.

6.3.1.4 Corrosion Analysis of PEG-4000:

- As an additional step, the corrosion behaviour of PEG-4000 in contact with various container materials, namely "Copper (Cu), Aluminium (Al), and

Stainless Steel (SS)”, is examined. Test samples measuring 10x30 mm^2 are utilized for this investigation.

- The metal specimens undergo a thorough cleaning process with ethanol and acetone for 10 minutes and are then subjected to a hot air oven at 80°C for an additional 10 minutes to eliminate impurities and moisture.
- Subsequently, each of the three metal samples is individually placed in separate test tubes and fully immersed in PEG-4000 PCM.
- These samples undergo heating and cooling for 1000 thermal cycles. Following the thermal cycling, they were removed and cleaned with acetone and ethanol.
- They are then dried in a hot air oven at 80°C for 10 minutes to eliminate residual moisture. The final weight of each metal sample is measured to assess any changes.
- The corrosive impact of PEG-4000 PCM on the three metal samples is evaluated by calculating the % weight loss in each case.

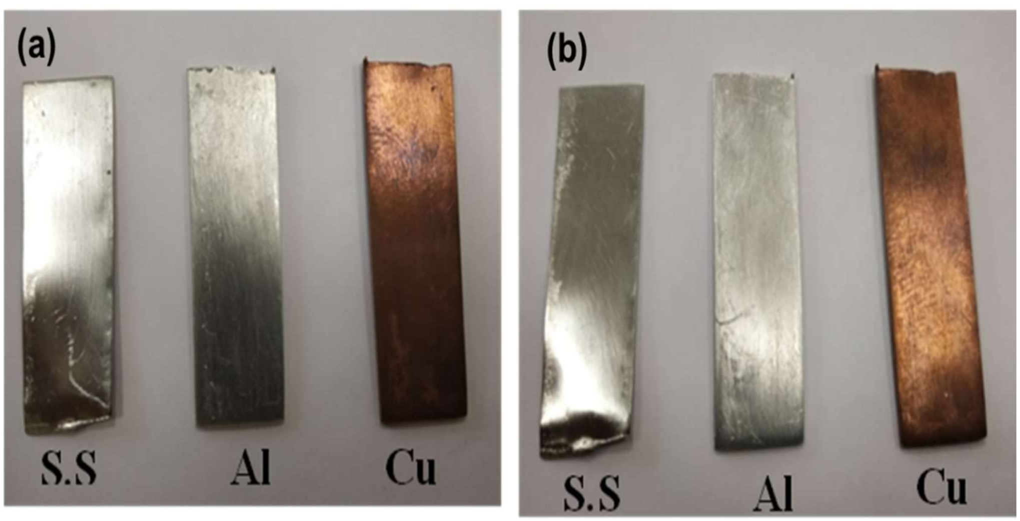


Figure 6.44: (a) Corrosion of metal samples before and (b) after corrosion

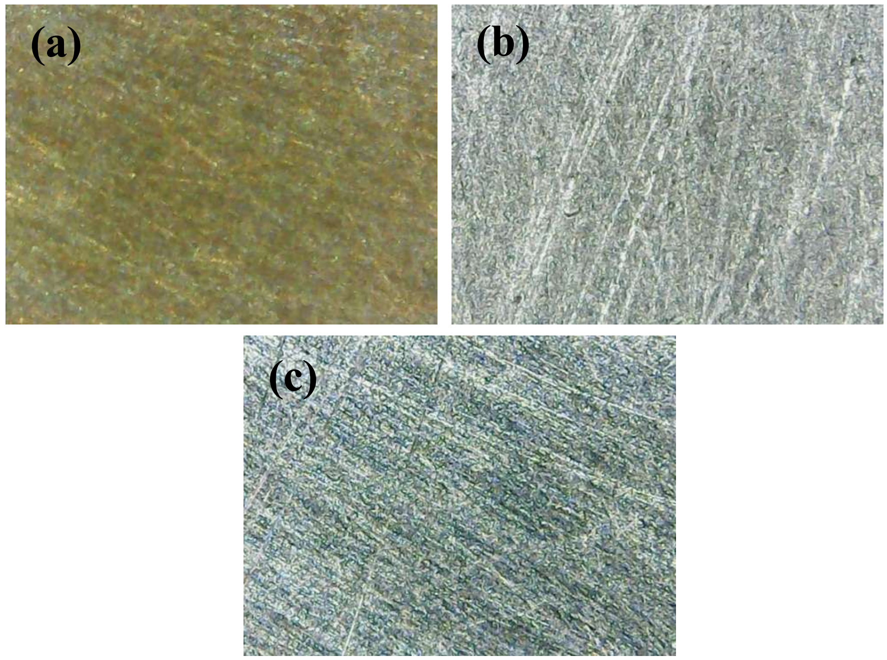


Figure 6.45: Optical image of (a) Copper, (b) Aluminium and (c) Stainless Steel metal samples after charging and discharging cycles

Corrosion within the PCM container can significantly impair and shorten the lifespan of the latent energy storage system. Since each PCM exhibits distinct corrosive properties toward container materials, it is imperative to investigate the corrosion behavior of PCM on these materials. To this end, the corrosion properties of PEG-4000 on aluminum, stainless steel, and copper were examined using the gravimetric analysis method. The total mass loss of the metal specimens was determined using the following formula,

$$\Delta m = m(t_o) - m(t_1) \qquad ………..(2)$$

Where $m(t_o)$ is the initial weight of the metal samples and $m(t_1)$ is the finial weight of the metal samples after thermal cycle. The percentage weight loss was calculated with respect to total mass loss of metal sample (Δm). The percentage weight loss of the metal samples was calculated by the following expression [83],

$$\%\ \text{Weight loss} = \Delta m / m(t_o)\ \times 100\ \% \qquad ……………………..(3)$$

The percentage weight loss was calculated with respect to total mass loss of metal sample (Δm).

Table 6.8: Percentage weight loss of metals samples in PEG-4000

S. No	Type of material (PEG 4000)	Initial weight (g)	Final weight (g)	Total weight loss (g)	Percentage weight loss (%)
1	Aluminium	0.627	0.624	0.003	0.478
2	Stainless steel	0.840	0.838	0.002	0.238
3	Copper	2.482	2.478	0.003	0.12

To ensure long-lasting energy storage systems, PCM containers are chosen based on percentage weight loss. Materials are classified into three categories: 'caution,' 'not recommended,' and 'recommended. Materials falling under the recommended category exhibit minimal corrosion, indicating suitability for long-term service without the need for replacement. The initial weights of aluminum, stainless steel, and copper are 0.627g, 0.840g, and 2.482g, respectively. The percentage weight loss was calculated using formula 3. The weight loss percentages of the metal samples are determined by dividing the total weight loss of the metal specimens by the initial weight of the metal samples. table 6.8 presents the percentage weight loss of the metal samples due to PEG 4000 after thermal charging and discharging cycles.

We examined the corrosion resistance of different metals. Aluminum experienced the highest weight loss (0.478%). Stainless steel showed moderate weight loss (0.238%). Copper exhibited the lowest weight loss (0.12%). The results of weight loss of metal samples were benchmarked against industrial standards for corrosion analysis, as depicted in table 6.9. The corrosion studies conducted on aluminum, copper, and stainless steel with PEG 4000 indicate that all three container materials are suitable for latent thermal energy storage applications without necessitating replacement.

Table 6.9: Reference for weight loss analyses used in industry

Weight loss	"Recommendation"
> 50%	"Destroyed within days"
10-50%	"Not recommended for service greater than a month"
5-10%	"Not recommended for service greater than one year"
1-5%	"Caution recommended, based on the specific application"
0.5-1%	"Recommended for long term service"
<0.5%	"Recommended for long term service; nearly no corrosion"

6.3.1.5 Thermal and chemical stability studies of PEG 4000:

Thermal stability is a critical parameter for PCM to determine the material decomposition at different temperature. The TGA curve of PEG-4000 is shown in Figure 6.46. The result exhibits that the decomposition of PEG starts at 200°C and completely decomposes at 400 °C. The sharp weight loss can be attributed to the breakdown of organic components and only 0.1 % of residue was attained at 500 °C. The PEG-4000 has good thermal stability as the degradation starts at 200 °C and therefore suitable for the TES application.

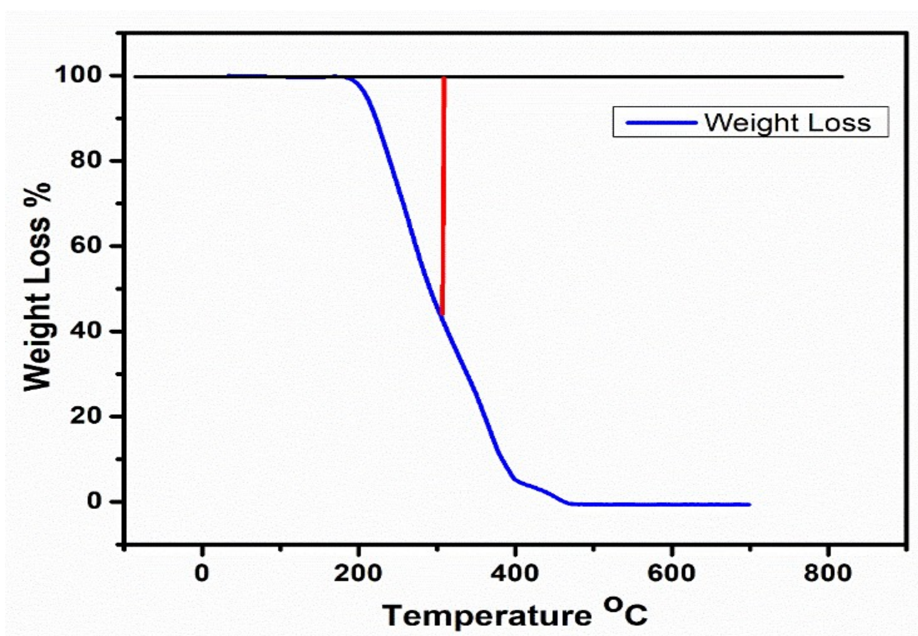


Figure 6.46: TGA curve of pure PEG-4000.

6.3.1.6 FTIR Analysis:

The FTIR spectra of pure and after 1000 thermal cycles of PEG is shown in Figure 6.47. The typical distinctive peaks at 2898 cm-1, 947 cm-1 and 846 cm-1, matches to stretching vibration of the -CH2 functional group. The peak at 1105 cm-1is due to the C-O stretching vibration of the functional group. Moreover, the characteristic peak at 1471 cm-1, 1353 cm-1 is due to the deformation vibration of the C-H bond, the bending vibration of the O-H group at 1279 cm-1. The absorption peak at 3415 cm-1 is due to the -OH functional group. FTIR spectra of PCM were identical before and after 1000 thermal cycles and therefore it is confirmed that no chemical degradation of the PCM is ensued. This result indicates PEG 4000 has good chemical stability and can be effectively used for extended tenure of TES application.

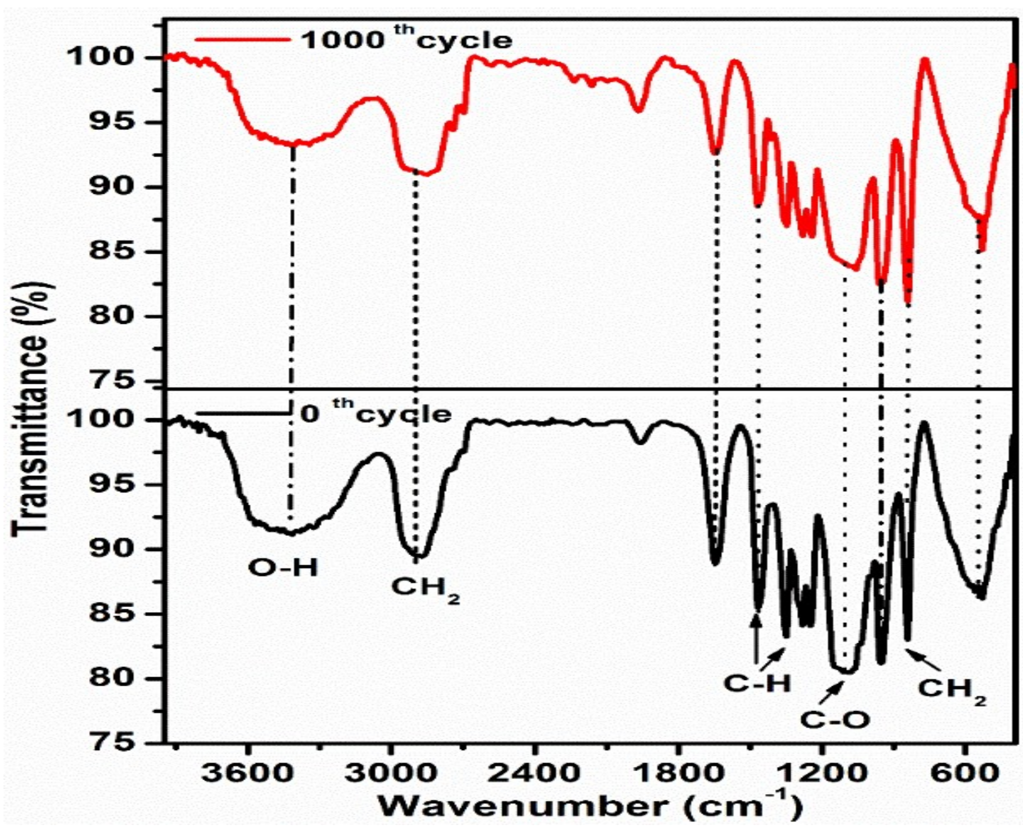


Figure 6.47: FTIR spectra of 0th and 1000th cycle of PEG-4000

Table 6.10: Results of Material Characterization for Heat Exchanger

Parameter	This work
Phase Change Material (PCM)	**Polyethylene Glycol (PEG 4000)**
Melting point (°C)	**58-60**
Density at 60 °C (g/cm^3)	**1.092**
Latent heat of fusion (J/g)	**150.8**
Heat Capacity (J/g)	**171.1**
Thermal cycle time (minutes)	**25**
Transition temp. RPD maximum (%)	**1.66**
Latent Heat of Fusion RPD maximum (%)	**1.92**
Weight loss (%) of container metal (Cu, SS, Al)	**0.121-0.478** (<0.5%)
Therma stability	**No weight loss up to 200 °C**
Chemical stability	**Stable for at least 1000 cycles**
Suitable for device fabrication	**Yes/Long lasting**

6.3.2. Heat Exchanger Device Performance Evaluation

6.3.2.1 Charging Characteristics:

The influence of mass flow rate on heat storage features of shell and tube heat exchanger with PEG-4000 is studied. The shell and tube heat exchanger are filled with PEG-4000 PCM. The charging of the PCM experiment is carried out in 3 different mass flow rate 3 kg/min, 4 kg/min and 6 kg/min. The temperature of PCM is measured at regular intervals of time to study the charging behavior of PCM. Figures 6.48, 6.49 and 6.50 show the temperature profile of PCM inside the heat exchanger at different mass flow rate.

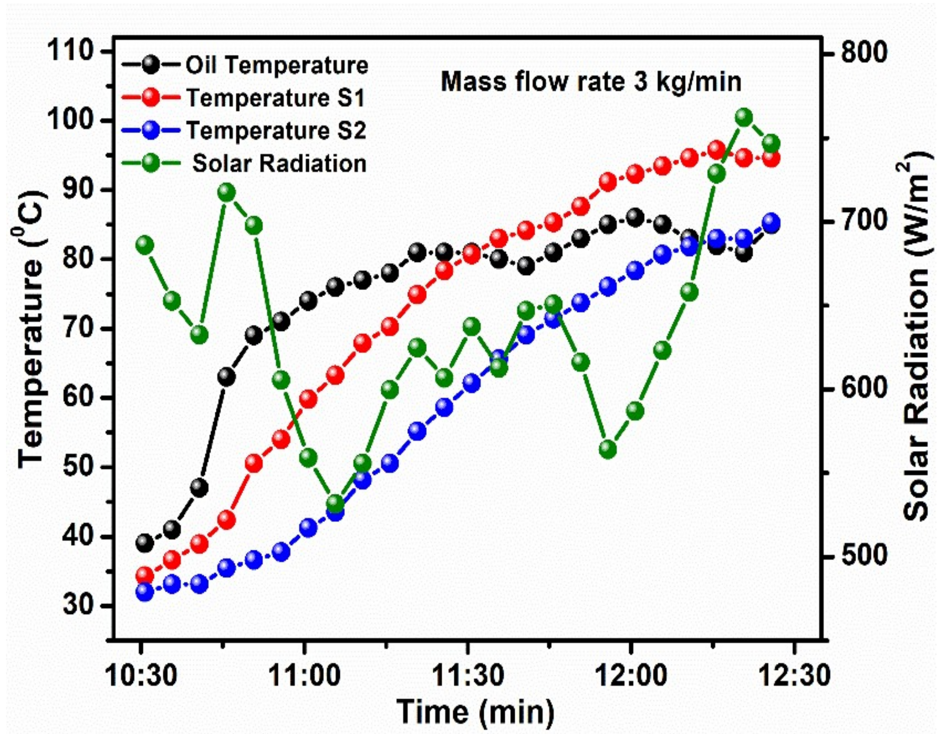


Figure 6.48: Temperature profile of PCM during charging at mass flow rate 3 kg/min.

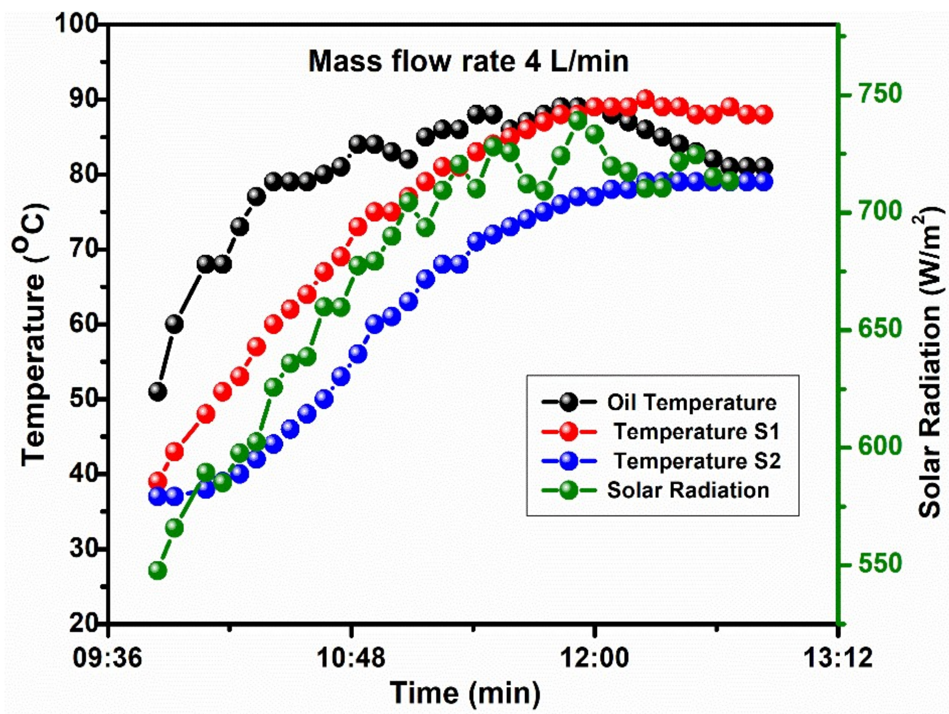


Figure 6.49: Temperature profile of PCM during charging at mass flow rate 4 kg /min.

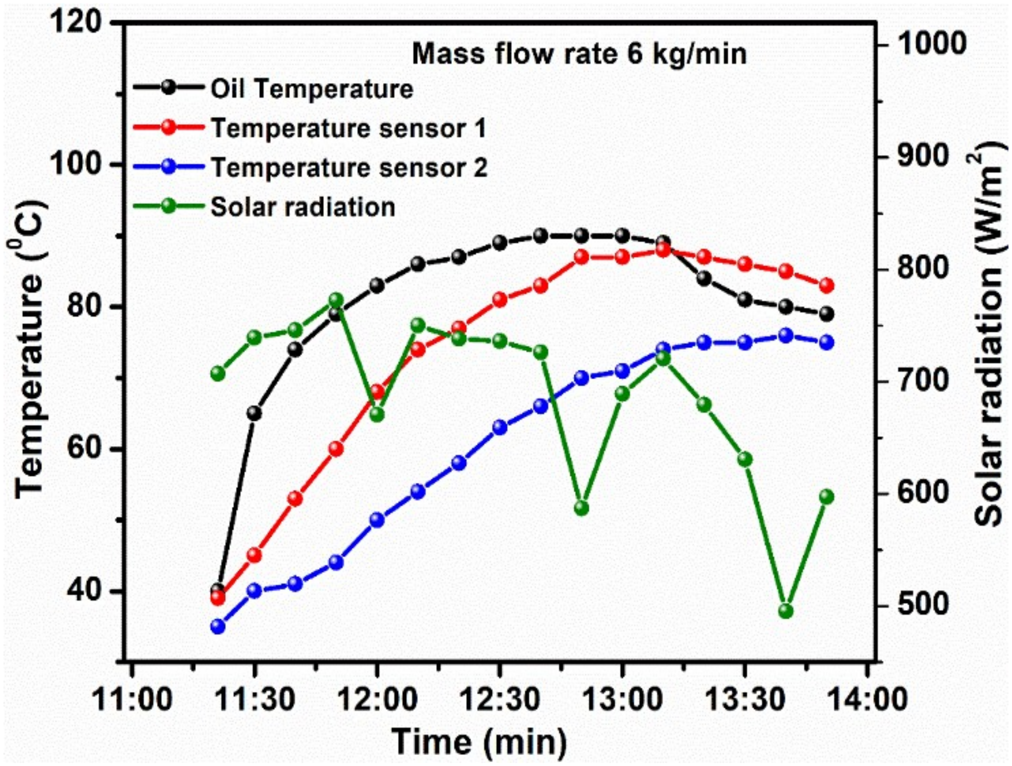


Figure 6.50: Temperature profile of PCM during charging at mass flow rate of 6 kg/min.

The total time required to charge the PCM from 35 to 70℃ in shell and tube exchanger at different mass flow rate is 3, 4 and 6 kg/min is 45 mins, 65 mins and 85 mins. The experimental result shows that mass flow rate of HTF influences the PCM phase change rate in heat exchanger. Usually, PCM have low thermal conductivity property in solid phase and large thermal conduction resistance during heat transfer from HTF to PCM. By convective heat transfer process, the HTF mass flow rate is directly proportional to convective heat transfer coefficient between Wall and HTF fluid. By this reason the thermal resistance between wall and HTF is reduced during convective heat transfer process.

6.3.2.2 Discharging Characteristics:

The effect of mass flow rate on discharging characteristics of latent heat storage system is studied for HTF mass flow rate in water stagnation condition, 2.2 kg/min and 4 kg/min. From figures 6.51, 6.52 and 6.53, it shows that temperature profile during discharging process. A sharp decrease in temperature profile of PCM is shows at initial stages of discharge process which continues until the PCM started to freeze (solidify) which shows that heat transfer process is dominated by thermal conduction between the HTF and tube during the solidification process. The total time taken to discharge thermal energy from PCM to reach 40 °C is 360 min when water is maintained at stagnation condition. Similarly, the total time required to discharge thermal energy from PCM is 20 min and 15 min for mass flow rate of 2.2 kg/min and 4 kg/min. The results show that the discharging time is reduced when the flow rate of HTF increases.

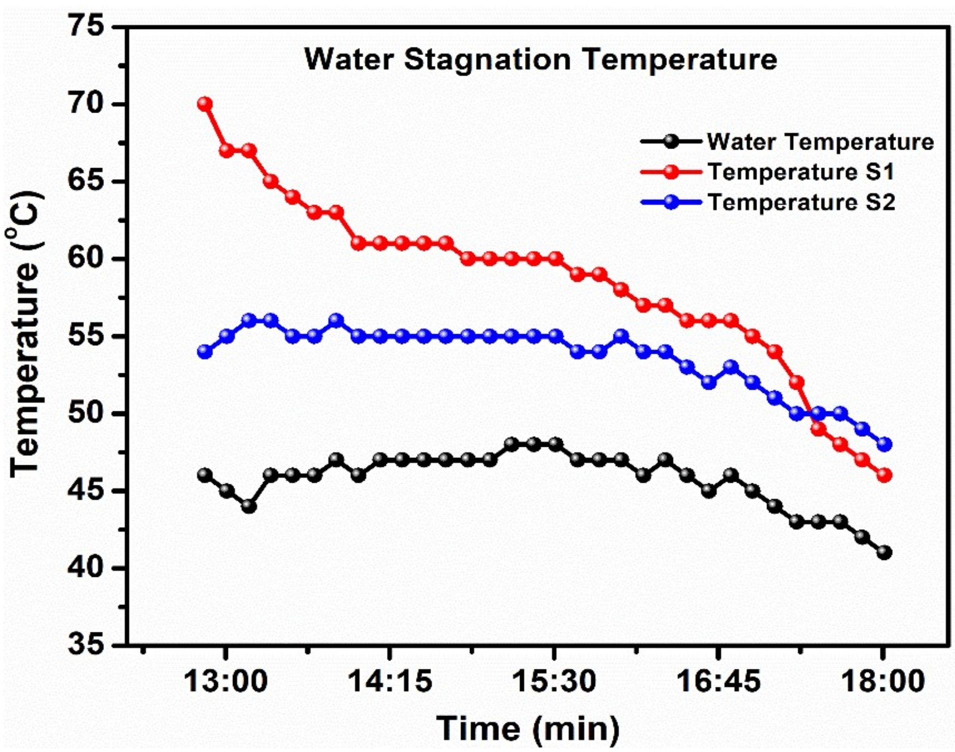


Figure 6.51: Temperature profile during discharging at water stagnation condition.

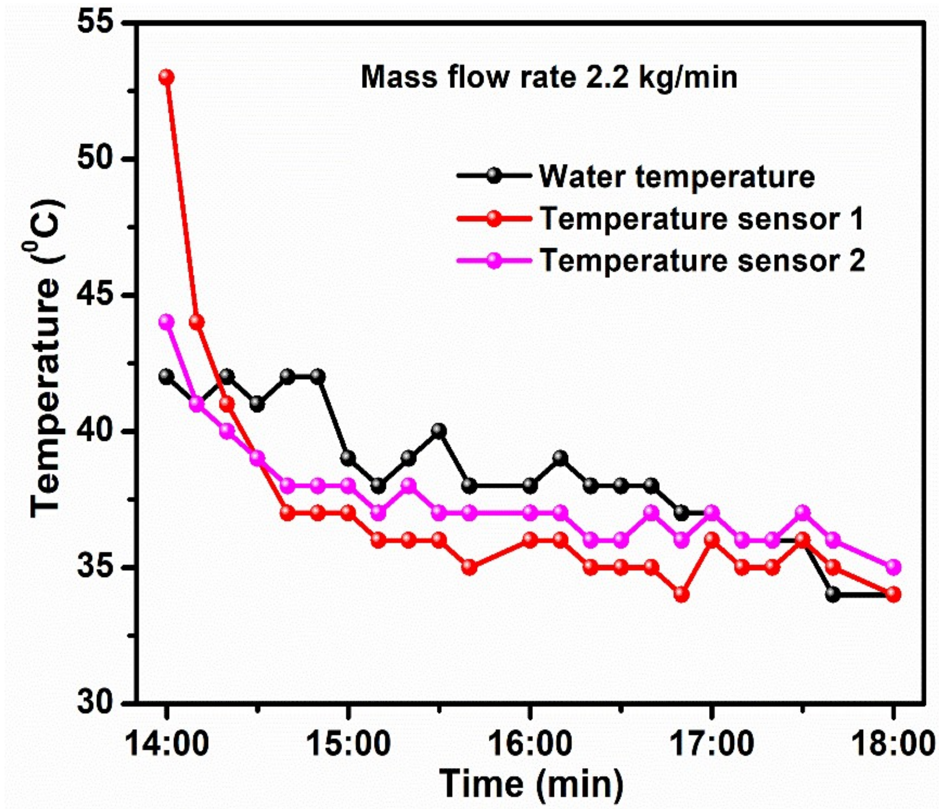


Figure 6.52: Temperature profile during discharging at mass flow rate of 2.2 kg/min.

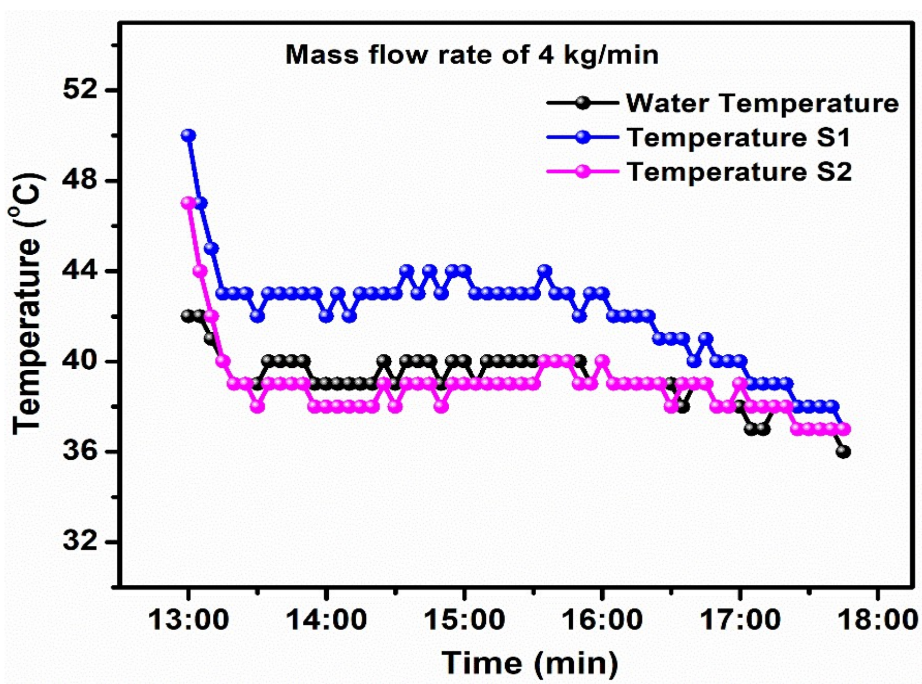


Figure 6.53: Temperature profile during discharging at mass flow rate of 4 kg/min.

6.3.2.3 Comparison of Charging and Discharging properties:

TES exhibits a key role in energy generation and conservation of non-conventional and conventional energy resources. PEG-4000 an organic PCM is identified for low temperature LHTES application. The thermal reliability, chemical stability, thermo-physical properties and corrosion features of PCM are studied by accelerated thermal cycle test. The studies showed that RPD value of LHF and melting temperature of PEG 4000 at one thousand cycles is -1.92% and -1.66%. The variation in LHF and melting temperature of PEG 4000 is minimum compared to zeroth cycle.

The compatibility study of PEG 4000 PCM with copper, aluminium and stainless-steel container is studied and the result of corrosion test shows corrosion of all three metal samples is recommended for long term services. The results indicate that this PCM has good thermal stability over a long-term usage, could be effectively used for long term thermal storage application. A Shell and tube heat exchanger is developed to study the heat transfer characteristics of latent heat thermal storage system for both discharging and charging process of identified organic phase change material. The thermal charging duration for mass flow rate of 3, 4 and 6 kg/min is 45, 65 and 85 min. Similarly, the discharging process with different mass flow rate of 2 and 4 kg/min is 20 and 15 min.

Table 6.11: Results of Charging-Discharging characteristics of the Heat Exchanger

Charging characteristics		**Discharging characteristics**	
Mass flow rate of HTF oil (kg/min)	Heat from HTF to PCM. (35 to 70 ^{0}C) = Heating Time of charging (min)	Mass flow rate of water (kg/min)	Heat from PCM to water (70 to 35 ^{0}C) = Cooling Time of discharging (min)
3	45	0 (stagnated water)	360
4	65	2.2	20
6	85	4	15

Comments:

- Slow charging at higher MFR of HTF during heating of PCM.
- Solar radiation minor addition to heating, not much effect.
- Charging is consistent as both sensors show similar progress and in accordance with fluid temperature.
- Fast discharging at higher MFR of water during cooling of PCM.

Table 6.12: Comparative results of PEG-4000 Heat Exchanger

Parameter	Previous works materials used	This work
Phase Change Material (PCM)	Phenyl acetic acid, wax, glutaric acid etc. [59-72]	**Polyethylene Glycol (PEG-4000)**
Latent heat of fusion (J/g)	Upto 120	**150.8**
Heat Capacity (J/g)	Upto 100	**171.1**
Thermal cycle time (minutes)	30-50 (slow)	**25 (fast)**
Transition temp. RPD (%)	Upto 30 (high variations)	**1.66**
Latent Heat of Fusion RPD (%)	Upto 30 (high variations)	**1.92**
Weight loss (%) of container / Corrosion	1 to 5%	**0.121-0.478 % (nearly no container material loss)**
Thermal stability	No weight loss only upto 100^{o}C	**No weight loss upto 200^{o}C**
Chemical stability	Stable for upto 500 cycles	**Stable for atleast 1000 cycles**
Device condition	Ok/not long lasting	**Good/long lasting**

6.4 Conclusion of Results and Discussions

The study achieves its objectives by demonstrating significant advancements in energy storage technologies. Key conclusions include:

- **Supercapacitor Advancements:**
    - The Parali-based supercapacitor achieves an optimal balance between energy and power densities, addressing the limitations of traditional storage devices.
    - Its scalability and sustainability make it a viable solution for renewable energy integration and portable electronics.
- **TES System Contributions:**
    - The use of PEG-4000 as a PCM introduces a reliable and efficient thermal storage solution, suitable for both domestic and industrial applications.
    - The shell-and-tube heat exchanger design ensures consistent performance and long-term reliability.

These findings establish the innovative contributions of this research, offering transformative solutions to modern energy challenges.

Chapter 7. Conclusions

Electrical energy storage (EES) system derived from biomass exhibit promising energy density. The hierarchical porous and crystalline functional carbon, characterized by cylindrical features obtained from Parali biomass, boasts high carbon content and surface area. This activated carbon facilitates efficient ion and electron transport, enhancing the charge storage capacity within the electrochemical double layer.

Consequently, it serves as an excellent material for electrodes in electrical double layer supercapacitors, offering exceptional stability and coulombic efficiency. The resulting aqueous symmetric supercapacitor, employing activated carbon electrodes, achieves a notable energy density of 54 Wh/kg, coupled with excellent coulombic efficiency and stability. Furthermore, a laboratory prototype of the supercapacitor successfully powers a commercial electronic DC motor and an LED bulb for 12.5 and 14 minutes, respectively, on a single charge, demonstrating the potential of Parali biomass as a renewable and sustainable source for high-energy density storage systems in non-conventional energy applications.

- Agricultural waste product (Parali) was used to develop high energy density electrical energy storage system
- KOH and H_3PO_4 based activation was done with Parali for electrode of Supercapacitor for the first time.
- Eco-friendly approach
- Supports Waste management
- Simple method and results are good
- Cost effective electrical energy storage device
- More materials and methods can be explored

Thermal energy storage (TES) plays a pivotal role in both energy generation and conservation across conventional and non-conventional energy sectors. PEG 4000, an organic phase change material (PCM), emerges as a promising candidate for low-temperature latent heat thermal energy storage applications. Its thermal reliability, chemical stability, thermo-physical properties, and corrosion resistance were evaluated through accelerated thermal cycle tests.

Results indicate minimal relative percentage deviation (RPD) in the latent heat of fusion (LHF) and melting temperature of PEG 4000 after one thousand cycles (-1.92% and -

1.66%, respectively). Compatibility studies with copper, aluminum, and stainless-steel containers reveal a percentage weight loss of less than 0.5% for all the three, though copper being showing the lowest making it suitable for long-term service.

These findings suggest that PEG-4000 exhibits robust thermal stability over extended usage, rendering it suitable for long-term thermal storage applications. Additionally, a shell and tube heat exchanger were developed to investigate the heat transfer characteristics during the charging and discharging processes of the identified organic phase change material.

The thermal charging durations for mass flow rates of 3, 4, and 6 kg/min were determined to be 45, 65, and 85 minutes, respectively. Similarly, the discharging process durations for mass flow rates of 2 and 4 kg/min were found to be 20 and 15 minutes, respectively.

- Novel heat exchanger (Thermal energy storage system)
- Industrial Waste products and other materials utilized to make novel thermal energy storage device
- Eco-friendly approach
- Supports Waste management
- Simplest method and results are good
- Cost effective thermal energy storage device
- More materials and methods can be explored

Conclusively, novel Supercapacitor based on porous carbonaceous material electrodes designed and give good results. The energy density was enhanced without compromising the power density of the device. The best thermal energy storage device making material is PEG-4000. Novel Heat exchanger gave good results.

The supercapacitor gave good electrochemical and thermal results.

The space heater (heat exchanger) also gave good results.

Both the approaches were eco-friendly, simple and cost effective. Two Novel High Energy Density Storage Systems designed so far gave optimum results.

In points, the whole conclusion of the research work can be give as follows:

- Novel Supercapacitor based on porous carbonaceous material electrodes designed and give good results

- The energy density was enhanced without compromising the power density of the device
- The best thermal energy storage device making material is PEG-4000
- The supercapacitor gave good electrochemical and thermal results
- The space heater (heat exchanger) also gave good results
- Both the approaches were eco-friendly, simple and cost effective
- Two Novel High Energy Density Storage Systems designed so far gave optimum results

7.1 Overall Summary

- A model of supercapacitor was simulated on Matlab-Simulink was 'modelled and optimized' in Objective 01
- KOH and H_3PO_4 based activation was done with Parali and 'novel high specific surface area functional carbon' was synthesized and characterized in Objective 02
- "High energy density novel electrical energy storage device (Parali Supercapacitor)" was fabricated and studied in Objective 03
- "Novel thermal energy storage device (PEG-4000 Heat exchanger)" was fabricated and studied in Objective 04
- Prior simulation was done to save time and resources
- Agro-waste (Parali) was used for electrical energy storage material and device fabrication
- Chemical waste (PEG-4000) was utilized for thermal energy storage system fabrication
- Eco friendly approaches were incorporated
- Waste management was focused on
- Simple and cost-effective methods were followed

7.2 Significant Contribution of the Work:

This research provides substantial contributions across various sectors:

- **Government Policies:**
    - Supports waste-to-energy initiatives by utilizing agricultural waste, aligning with environmental goals and reducing air pollution.

- Encourages the adoption of renewable energy storage technologies in national energy policies.

- **Private and Industrial Applications:**
    - Offers cost-effective and scalable energy storage solutions for industries, reducing operational costs and carbon footprints.
    - Enhances energy efficiency in sectors like manufacturing, transportation, and renewable energy integration.
- **Agriculture and Rural Development:**
    - Promotes sustainable practices by converting agricultural residues like Parali into high-value energy storage materials.
    - Provides energy solutions for rural areas, supporting agricultural mechanization and reducing dependence on traditional energy sources.
- **Research and Academia:**
    - Opens new avenues for interdisciplinary research in material science, renewable energy, and waste management.
    - Provides a framework for future studies on hybrid energy storage systems and advanced material applications.
- **Global Energy Sector:**
    - Addresses energy security challenges by offering scalable and sustainable solutions for renewable energy integration.
    - Contributes to global efforts in reducing greenhouse gas emissions and promoting sustainability.

These contributions demonstrate the far-reaching impact of this research, advancing the fields of energy storage, sustainability, and environmental protection.

Chapter 8. Future Scope of the Research

More materials and methods can be explored in eco-friendly way.

Activated carbons can be explored more like in composites e.g. Metal composites or carbon nanocomposites for making electrodes of supercapacitor or other energy storage devices. Parali can be further investigated to make other energy storage devices like batteries, capacitors, supercapacitors etc. More biomasses can must be explored and more activation procedures can be adopted to better improve the carbon content and purity of the material to be used as energy storage systems. Modelling and simulation of more models can be done.

On the other as far as thermal energy storage systems are concerned, more materials not only the chemical wastes but other waste materials from other fields can be investigated for making of thermal energy storage systems and other systems can be made. Eco friendly approach must be followed as has been done in this project for making energy storage systems. More mass ratio variation with different activation agents can be used for parali. More chemical and other wastes can be utilized for heat exchanger and hybrid systems can be implemented as well. More materials and methods can be explored in eco-friendly way.

- Different activation agents can be explored
- Different ratios of activation agents like KOH and H_3PO_4 can be explored
- Different biomasses can be explored
- Different activation methods can be explored
- Matlab simulation for different parameters can be done
- Biomass waste and chemical waste can be explored more for electrochemical and thermal properties
- More phase change materials and activated carbons can be explored
- Hybrid systems of energy storage can be further studied and incorporated

8.1 This Research Topic as the Need of Today in area of Energy Storage

Energy storage has become a critical focus area in today’s energy landscape due to the following global challenges:

➢ Intermittency of Renewable Energy Sources: Renewable sources such as solar and wind energy are inherently variable and unpredictable. Efficient energy storage systems are essential to store surplus energy during peak production periods and release it during low-generation times.

- This research addresses this issue by developing a novel supercapacitor capable of bridging the gap between batteries (long-term storage) and capacitors (high-power delivery). Additionally, the thermal energy storage (TES) system based on PEG-4000 ensures efficient storage of heat from solar energy, making it available for industrial or domestic use during non-peak hours.

➢ Environmental Concerns: The growing need to minimize reliance on fossil fuels and reduce greenhouse gas emissions has driven the search for sustainable alternatives. This research utilizes Parali biomass, an agricultural residue often burned in regions like Punjab, causing severe air pollution, as a precursor for high-performance supercapacitors.

- This aligns with the global push toward circular economies and waste-to-energy practices, promoting environmental sustainability.

➢ Technological Advancements in Energy Systems: Emerging industries like electric vehicles (EVs), portable electronics, and smart grids require energy storage systems with high power density, fast charging rates, and long lifespans.

- The developed supercapacitor offers a balance of energy and power densities, making it suitable for these applications. Similarly, the TES system provides efficient heat storage, addressing the needs of industries requiring reliable thermal energy solutions.

➢ Energy Security: With depleting fossil fuels and fluctuating global energy markets, the need for localized and renewable energy storage systems has never been greater. This research offers practical, scalable solutions that enhance energy security while supporting sustainable development.

In summary, this research is timely and addresses key issues in the energy sector, offering sustainable, efficient, and scalable solutions to modern energy challenges.

8.2 Significances of the Research Work for Advancement of Science, Industry and Society

The research has profound implications across multiple domains, bridging the gap between scientific advancements, industrial innovation, and societal benefit:

- For Science and Technology:
  - Material Science Advancements: The synthesis of activated carbon from Parali biomass demonstrates how agricultural residues can be converted into high-performance materials for energy storage, opening new avenues for material science research. The innovative use of PEG-4000 as a Phase Change Material (PCM) in TES systems contributes to the field of thermal energy storage, particularly in optimizing phase change properties for real-world applications.
  - Improved Energy Storage Metrics: The supercapacitor achieves significant improvements in specific capacitance (247.6 F/g) and energy density (54 Wh/kg), contributing to the development of hybrid energy storage systems. The TES system demonstrates long-term thermal reliability with negligible degradation, providing a benchmark for future studies in this area.
- For Industry:
  - Biomass Gasifier Manufacturers: This research provides a framework for converting biomass into high-value energy storage materials, enabling gasifier manufacturers to diversify their offerings and increase the value chain.
  - State Energy Development Agencies: Agencies can adopt these technologies to promote decentralized energy systems, reducing dependence on centralized power grids and promoting renewable energy integration.
  - Municipal Corporations: The waste-to-energy approach can be extended to municipal waste management, converting organic waste into materials for supercapacitor electrodes or thermal energy storage applications.
  - Farm Owners and Agricultural Sectors: Farmers can benefit from a sustainable solution to Parali disposal, reducing air pollution caused by stubble burning and generating additional income streams from agricultural waste.

- Renewable Energy Sector: The developed systems are ideal for renewable energy applications, such as storing solar and wind energy, thereby improving the efficiency and reliability of renewable energy systems.

➢ For Society:

- Environmental Benefits: Reducing stubble burning and promoting the use of renewable energy storage systems contribute to cleaner air, mitigating health risks and environmental damage.
- Energy Access: Scalable and cost-effective energy storage solutions ensure energy access in rural and underdeveloped areas, fostering economic growth and improving living standards.
- Sustainable Development Goals (SDGs): The research aligns with SDGs such as affordable and clean energy, sustainable cities and communities, and climate action, contributing to global sustainability efforts.

By addressing critical needs across these domains, the research establishes a strong foundation for the advancement of energy storage technologies, benefiting science, industry, and society.

8.3 Appendix of Commissioned Biomass Power Projects in Punjab[138]

Sr. No.	Company	Location	Capacity (MW)	Biomass burnt (MT/annum)	Technology Used	CO_2 Emission (MT/annum)
1	M/s. Malwa Power Ltd.	Muktsar	6	54,000	Direct Combustion	~25,000 - 35,000
2	M/s. Dee Development Engineers Pvt. Ltd	Fazilka	8	72,000	Direct Combustion	~35,000 - 45,000
3	M/s. Universal Biomass Energy Pvt. Ltd.	Muktsar	14.5	1,30,500	Direct Combustion	~65,000 - 90,000
4	M/s. Green Planet Energy Pvt. Ltd.	Hoshiarpur	6	54,000	Direct Combustion	~25,000 - 35,000
5	M/s. Green Planet Energy Pvt. Ltd.	Jalandhar	6	54,000	Direct Combustion	~25,000 - 35,000
6	M/s. Viaton Energy Pvt. Ltd.	Mansa	10	90,000	Direct Combustion	~45,000 - 60,000

7	M/s. Green Planet Energy Pvt. Ltd.	Hoshiarpur	4	36,000	Direct Combustion	~18,000 - 25,000
8	M/s. Green Planet Energy Pvt. Ltd.	Moga	6	54,000	Direct Combustion	~25,000 - 35,000
9	M/s. Sampuran Agri Venture Pvt. Ltd.	Fazilka	1	8,000	Direct Combustion	~4,000 - 6,000
10	M/s. Sukhbir Agro Energy Limited	Faridkot	18	1,62,000	Direct Combustion	~80,000 - 110,000
11	M/s. Sukhbir Agro Energy Limited	Ferozepur	18	1,62,000	Direct Combustion	~80,000 - 110,000

Table 8.1: Appendix of Commissioned Biomass Power Projects in Punjab by PEDA (Punjab Energy Development Agency)

The establishment of biomass-based power plants in Punjab represents a significant step towards addressing the environmental concerns associated with the open burning of agricultural residues, particularly paddy straw/parali. The direct burning of Parali in Punjab and neighbouring Haryana is a major contributor to air pollution in North India, leading to severe environmental and health issues. In response, the government has initiated and commissioned several biomass-based power plants, as detailed in the table above, which utilize paddy straw and other agricultural residues as their primary raw material.

While these power plants contribute to waste-to-energy conversion, they predominantly rely on direct combustion technology, which, although cleaner than coal-based thermal power plants, still results in significant CO_2 emissions, as indicated in the last column of the table, the environmental impact.

To enhance the sustainability of biomass utilization, this thesis explores alternative, environmentally friendly approaches that optimize biomass usage, particularly parali, beyond direct combustion. The proposed solutions offer a more sustainable pathway (activated carbon instead of burnt carbon), reducing net CO_2 emissions while maximizing energy efficiency and resource utilization. This will mitigate the issue of parali burning and can provide pathway in using the chemical wastes also in this field of energy storage technology in terms of electrical and thermal energy storages.

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List of Publications

1. Yaquin H., and Dheep G. R., "Review on Materials and Methods for Supercapacitors", in Proc. 2020 3rd Int. Conf. Intell. Sustain. Syst. (ICISS), 2020, pp. 1-5, doi: 10.1109/ICISS49785.2020.9315859.
2. Yaquin H., and Dheep G. R., "Influence of fabrication parameters and optimization of supercapacitor – A simulation analysis", J. Phys.: Conf. Ser., vol. 2327, 012014, 2022, doi: 10.1088/1742-6596/2327/1/012014.
3. Yaquin H., Dheep G. R., and Verma Y. K., "Fabrication and development of a biomass-based supercapacitor with enhanced energy storage characteristics", ECS J. Solid State Sci. Technol., vol. 13, no. 2, p. 021003, Feb. 2024, doi: 10.1149/2162-8777/ad2553.
4. Patent titled "Novel Materials Based Energy Storage Systems", bearing registration number 'L-162005/2025' at Indian Patent Office, inventors – Haziqul Yaquin & Dr. G. Raam Dheep. (March 3, 2025)
5. Book Chapter titled "Design and Development of High Density Energy Storage System for Renewable Energy Applications" by Haziqul Yaquin & Dr. G. Raam Dheep in the book 'Green Energy: A new Era for Power Generation', Apple academic press (2025).