ACTIVATED CARBON ELECTRODES FROM SUSTAINABLE RESOURCES FOR ECONOMICAL SODIUM SULFUR BATTERIES

By

Hooria Yaqub
Rija Hadi
Irha Sheikh

School of Chemical and Materials Engineering

National University of Sciences and Technology

2022

ACTIVATED CARBON ELECTRODES FROM SUSTAINABLE RESOURCES FOR ECONOMICAL SODIUM SULFUR BATTERIES

By
(Leader – 265254 Hooria Yaqub)
(Member 1 – 258505 Rija Hadi)
(Member 2 - 246248 Irha Sheikh)

A THESIS

Submitted to
National University of Sciences and Technology
In partial fulfilments of the requirements
for the degree of
METALLURGICAL AND MATERIAL ENGINEERING

School of Chemical and Materials Engineering

National University of Sciences and Technology

June, 2022.

CERTIFICATE

This is to certify that work in this thesis has been completed by Ms. Hooria Yaqub, Ms. Rija Hadi , and Ms. Irha Sheikh under the supervision of Dr. Zeeshan Ali and Dr. Salman Raza Naqvi at the school of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

--	----------------------------------
Advisor:	Co-Advisor (if any)
Dr Zeeshan Ali Department of Materials Engineering School of Chemical and Materials Engineering National University of Sciences and Technology	Dr. Salman Raza Naqvi Department of Materials Engineering School of Chemical and Materials Engineering National University of Sciences and Technology

Submitted Through:

HOD-------------------------------------

Department of Materials Engineering
School of Chemical and Materials Engineering
National University of Sciences and Technology

Principal/Dean -----------------------
School of Chemical and Materials Engineering
National University of Sciences and Technology

Abstract

The aim of this study is to attain sustainability and meet the increasing energy demands of the society. Sources of required materials for these batteries are cheaply and abundantly available in Pakistan. This project has led to development of one of these materials which is "activated carbon" that can be used as an anode material. This activated carbon is achieved using the hybrid methodology resulting in an optimum route with milder conditions. Activated carbon is an ideal material as anode of these batteries because it stores charge at millivolt ranges which is close to ideal as anode must store charge at minimal voltage to gives a highly efficient battery. As a result, these batteries would have a high storage capacity, high energy density, wide temperature operate ability and would be low cost. This development would further lead to electrification of off grid population of Pakistan and reliable energy resource for on grid population. Moreover, due to the sustainability factor, adverse environmental effects of coal fired thermal energy plants would reduce as well as burning of agricultural wastes in open fields resulting in dangerous smog and direct fuel combustion would decrease.

DEDICATION

Dedicated to our exceptional parents and respectful teachers whose tremendous support and cooperation led us to this wonderful accomplishment.

ACKNOWLEDGEMENT

We would like to pay gratitude towards Almighty Allah to guide us throughout this work at every step, opening new doorways of success for us, enlightening us with the knowledge and showering upon us His blessings which enabled us to achieve this success.

We are also extremely thankful to our supervisor Dr. Zeeshan Ali for his help during the project, his constant guidance and encouragement. The project would not have been possible without his expert advice, unfailing patience, and invaluable efforts.

We would also like to mention Mr. Ali Arshad for his incredible provision and assistance. We appreciate his guidance throughout the whole project.

Finally, we would also thank SCME and our project coordinators who walked us through all the administration related affairs.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

IEA International Energy Agency
RT Room Temperature
EDLC Electric Double Layer Capacitance
CVD Chemical Vapor Deposition
BET Brunauer-Emmet-Teller
NaSBs Sodium Sulfur Batteries
SEM Scanning Electron Microscopy
kWh Kilowatt hours
LIBs Lithium ion Batteries
NMC Nickel Manganese Cobalt
LFP Lithium Iron Phosphate
ASTM American Society for Testing and Materials
ACs Activated Carbons
KOH Potassium hydroxide
KCl Potassium Chloride
$ZnCl_2$ Zinc Chloride
Psi Pound-force per square inch
$KHCO_3$ potassium bicarbonate
$Na_3PO_4.H_2O$ trisodium phosphate dodecahydrate
$CO(NH_2)_2$ Urea
GCD galvanostatic charge discharge

CHAPTER 1

INTRODUCTION

Energy demands are rising every year due to massive population growth. This has led the masses to focus mainly on the fuels particularly fossil fuels such as oil, gas, and coal. After industrial revolution all the power plants installed consumed fossil fuel as the major energy source. According to the International Energy Agency(IEA) fossil fuel reserves are limited and have a lifespan of nearly 40-50 years. After that world would be devoid of major energy needs if suitable sustainable paths are not adopted. Moreover, the fact these fossil fuels are exhaustible, they are also deteriorating the environment one way or the other, for example, the emission of carbon dioxide gas, a major reason for global warming and ozone layer depletion.

1.1 Background

According to IEA globally 80% of electricity is generated using fossil fuels in recent time. Electricity generation in 2020 was 25.8T-kWh and in 2040 it is expected to reach 36.5T-kWh[1]. This estimates the electrical energy needs to rise about 70% until 2040 due to increase commercialization and urbanization. Thus, adopting a sustainable and environmentally friendly energy sources is the need of the time. This has got a major attention in the past two decades and engineers are working more on it to focus on using such resources which are not only surplus but also do not collide with the environment and assure a secure future.

1.2 Problem Statement

"Absence of Economical Anode Material to Be Used in Sodium Sulfur Batteries for Energy Storage Applications"

1.2.1 Problem Description

Pakistan is one of the most populated countries in south Asia, contributing approximately 2.56% of the total globe population. Since 2006 Pakistan has been facing severe energy shortfalls giving one of the lowest electrification rates (71%) in the region. Owing to the major energy deficiencies, the country face daily black outs and shutdowns (load shedding) at the peak hours of 13-14 hrs. in urban areas and 16-19 hrs. in rural areas[1]. Around 144 million people lack reliable access to the grid and 51 million are not even connected to the grid, considering most of them resides in the rural areas. This scenario has drastically affected the economic conditions of Pakistan, as most of the entrepreneurs and industrialists have moved their businesses to the neighboring countries. With rising population, increased industrialization and urbanization, this voracious thirst for energy is projected to further rise in coming decades. Hence short- and long-term measures are required to solve the existing energy crises in Pakistan. This calls the need of renewable and sustainable energy resources like sunlight based photovoltaic cells, wind power and tidal resources which could be the ultimate solution to address Pakistan's prevailing energy crises but depending primarily on the ecological conditions is where electrical energy storage devices are helpful in providing reliable and livable energy supply to the electricity grid from renewable means. [12]

Energy storage devices, especially batteries, are an indispensable unit of this technology for continuous provision of power specially in off-timings of solar and wind farms.

1.2.2 Sodium Sulphur Batteries

Sodium-sulfur batteries (NaSBs) can be considered as the most promising large-scale energy storage devices owing to their exceptionally high theoretical capacity, energy density, low cost and wide temperature range operate ability. It is very economical to produce them in Pakistan as the raw material is widely available, that is, sodium salts, sulfur deposits and carbon. The anode of the batteries is made from activated carbon which can easily be produced from biomass such coal, wheat straw, rice husk, coconut shells and cotton etc.

In our project we have used Rice husk. Pakistan is an agricultural country which produces 6-7million tons of rice per year and this makes rice husk to be cheaply available in Pakistan, which is the core material, producing activated carbon for sodium Sulphur batteries.

1.3 Purpose

The purpose of our project is to bring a possible route to solve the developing energy crises in Pakistan. Using the renewable energy resources, we aim to bring such batteries which are not only cheap and abundant but also has highest energy and power densities compared to the conventional batteries being used.

1.4 Scope

Scope of the project covers the application of producing cheap electricity through renewable sources, decreasing the carbon footprint, giving a sustainable path to use biomass waste, which will solve energy crises in future. This will make the people less dependent on fossil fuels (petrol, gasoline) and will pave the way to use clean and economical electricity, which is long lasting.

1.5 Project Objectives

Following are some of the crucial project objectives.

1.5.1 Establishing Suitable Route for Converting Agricultural Waste to Hard Carbon

Pakistan being an agricultural country produces a lot of agricultural waste but few value-added uses exist for their disposal whereas an extensive quantity is dumped in the landfills, doing no good and contributing to land and air pollution.
This waste normally includes nutshells(pecan, walnut, almost and coconut), fruit stones(apricot, peach, and cherry stones), grape seeds, wheat straw, citrus peel waste , bagasse, and corncob[13]. All these materials are renewable on an annual basis unlike other carbon containing raw materials, coal, wood, and peat etc. Limited research has been taken up in Pakistan regarding the production of activated carbon from agricultural waste but world is working in this field to achieve a promising and stable energy production technique. Our project holds a similar mission.

1.5.2 Decrease in carbon footprint by green utilization

Energy from fossil fuel generates a lot of carbon dioxide which is deleterious for the environmental. Renewable energy sources are a great replacement to these fossil fuels, among them biomass is a strong contender found almost every part of the world can be easily used for power generation and other energy applications. This is considered as an assuring source of energy for the production of electricity in near future. Biomass is considered as a prime importance because energy achieved from Biomass is carbon free as compared to the fossil fuels[15]. This complete shift can reduce the carbon dioxide up to 95%.

1.6 Preparing Activated Carbon for anode

Activated carbon is an amorphous, non-graphitic allotrope of carbon owing large surface area and pore volume, having functional groups and heteroatoms on the surface. These special properties make it an excellent absorbent, and is used in many industrial applications of filtration, purification, catalyst support and battery capacitor etc. Putting an end to the continuous consumption of graphite for battery electrode, major focus in made on the use of activated carbon for the battery system as the latter has high cyclic stability, energy, and power density than the former[17]. The micro and mesopores on activated carbon also hold great significance as they greatly improve the electronic structure and performance, shortening the transport length of cathode metal ions and bigger electrode/electrolyte interface for charge transfer action.

1.6.1 Pore Size and Distribution Control

Pore size and distribution control of activated carbon depends mainly on the type of precursor and activation method being used. Rice husk is a form of organic material containing 33.9% of carbon content. Though they contain high ash content but proper preparation parameters such as base and acid leaching of the precursor makes it able to produce high surface area activated carbon in an inert atmosphere. BET analysis measures the surface areas of activated carbon. For example, activated carbons produced from rice husk using H_3PO_4 and $ZnCl_2$ shows different specific surface areas such as 350-700m^2/g and 500-1200 m^2/g respectively[7]. Similarly, SEM results tell the morphology of the surface and gives an idea of porous or plane surfaces. Our project focuses on the objectives of obtaining optimal surface area and size distribution of activated carbon for coin cell assembly.

1.6.2 Coin Cell Assembly and Testing

Our Last objective focuses on the coin assembling of activated carbon as a cathode in a zinc metal electrode system. The electrolyte and binder selected should be compatible with our sample (activated carbon). This whole setup tells the voltage and charge capacity of our anode material which helps us to use it for Sodium Sulphur Batteries.

CHAPTER 2

LITERATURE REVIEW

2.1 Lithium-Ion Batteries

Lithium-ion batteries are great replacement to lead acid batteries as they are lighter, can store more charge and has a better battery life comparatively. Though in today’s world lithium-ion batteries are vastly used in all the gadgets including, laptops, iPod, cell phone, camera, and many more devices, still there is a high chance for lithium to explode any time as it is very reactive. Lithium-Ion batteries are mostly used for the purpose of producing electricity but they also associate some drawbacks which needs to be avoided, including the utilization of graphite anode which is limited and comes from a nonrenewable resource.

2.1.2 Types of Lithium-Ion Batteries

Lithium is a very reactive metal hence the electrode is manufactured from lithium salts which is extracted through mining. There are many types of lithium-ion batteries available in market, among them following are widely used Lithium Cobalt Oxide, Lithium Manganese Oxide, Lithium Iron Phosphate (LFP, Lithium Nickel Manganese Cobalt Oxide (NMC), Lithium Nickel Cobalt Aluminum Oxide, Lithium Titanate, Lithium Iron Phosphate (LFP). Our laptops and phones consist of Lithium Cobalt Oxide batteries. [14]

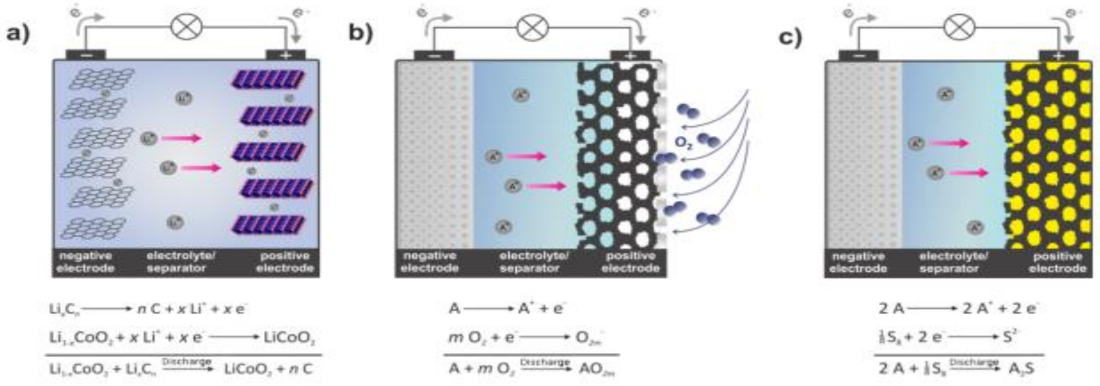


Figure 1: Operating principles of (a) a lithium-ion battery, (b) a metal–oxygen battery (non-aqueous electrolyte) and (c) a metal–sulfur battery during discharge. (A = Li, Na).

A lithium-ion battery is based on intercalation compounds as electrodes. The exact cell reaction depends on the materials used. In this example, the reaction equation is formulated for the classical LIB with graphite as the negative and $LiCoO_2$ as the positive electrode. The same concept can be applied for a sodium-ion battery. Metal–oxygen and metal–sulfur batteries perform best with a lithium or sodium metal as the anode. The positive electrode consists of a porous support, usually carbon. In a metal–oxygen battery, this support enables the reduction of atmospheric oxygen and accommodates the insulating discharge products of Li_2O_2, Na_2O_2, NaO_2, or ideally, Li_2O and Na_2O. In metal–sulfur batteries, the support hosts the insulating end members of the cell reaction, which are sulfur (before discharge) and ideally Li_2S and Na_2S (after discharge). The sketch in (b) illustrates the most frequently studied cell concepts for metal–oxygen and metal–sulfur cells. Other concepts, for example, solid electrolytes or liquid electrodes, are also currently being studied. [2]

2.1.2 Big Challenge

Every year billions of Lithium-ion batteries are produced which causes an immense consumption of graphite and would lead to scarcity of its resources in near future. Moreover, the traditionally used lithium-ion batteries have almost reached its theoretical limit which fails to meet the increasing needs for high storage capability , like grid energy storage and electrical vehicles. The electrochemical properties of LIBs mostly depend on graphite anode which has a specific surface area of 372mAh/g [17]. This low specific surface area offers a small site for electrochemical reactions and thus hinders its application for high storage charge system. For electric vehicles we need high power batteries which could run it for 10-12 hours and can charge in 10-15 mins[10]. Research is being carried out on lithium-ion batteries to improve the current technology but no such thing is invented now and this brings the need to test new materials and explore them. The poor power density of lithium-ion batteries hinders its application in the fields that require fast power delivery, such as accelerating and braking of vehicles. This leads the dire need to bring such storage devices which have high energy and power densities with sustainable and abundant resources.

2.2 Sodium Sulphur Batteries better than Lithium-Ion Batteries?

For more than 20 years lithium-ion batteries have been dominating over rechargeable battery market. This is due to their unparalleled energy density relative to others like nickel metal hydride, nickel chromium and lead acid batteries. However, the ongoing future demands to efficiently utilize renewable energy resources (non-fossil fuel) requires reversable grid scale battery system that can be built with abundant, environmentally friendly, and high energy storage electrode materials[18]. With this concept, Lithium ion batteries pose a serious concern due the shortage of its available resources, and intrinsically low power capacities of currently used lithium cathode system. The need for affordable, stationary energy storage has triggered intensive research in this field. The electrochemical energy storage with sodium and sulphur chemistries are gaining more and attention being low-cost technology for stationary energy storage application. The abundantly available reserves of sodium and Sulphur also makes them a long-lasting invention for the future. The sodium content in the earth's crust and water amount to 28,400 mg/kg and 11,000 mg/L compared to 20 mg/kg and 0.18 mg/L for lithium[2]. Moreover, the number of compounds of sodium are much larger than lithium.

2.2.1 RT Na-S battery

Sodium and Sulphur have a 50-year history in the use of electrochemical. However, the molten sodium operating at high temperature (above 300°C) pose a serious threat to safety, material cost and high temperature sealing as the use of the molten electrodes and ceramic electrolyte could be really deleterious. This resulted to use battery system with low temperature Na-S chemistry as a reliable alternative to smart grid system. A lot of difference regarding energy density is observed when replacing lithium ion with sodium ion batteries. The theoretical value for a room-temperature Na/S_8 battery with Na_2S as a discharge product (1.273 kWh/kg) and a Na/O_2 cell with Na_2O_2 as a discharge product (1.6 kWh/kg) are still very high compared to LIBs[2].

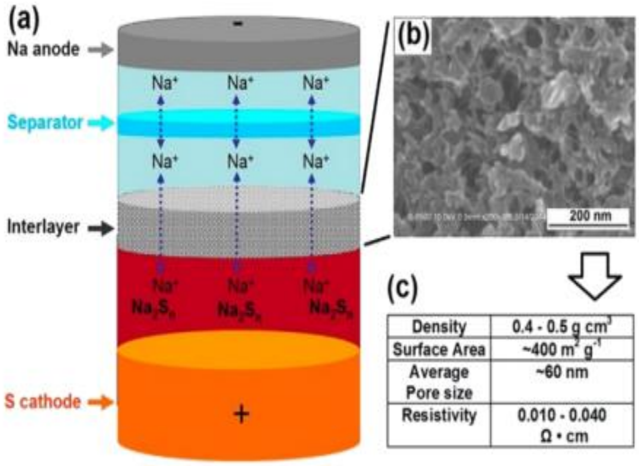


Figure 2: Room temperature sodium–sulfur battery based on shallow cycling between sulfur and soluble long chain polysulfides. An additional interlayer is used to reduce diffusion of polysulfides towards the sodium anode [2].

2.3 Lignocellulose based Bio-waste Materials derived Activated Porous Carbon

The prevailing concerns of scarce fossil fuels and global energy crises have lead scientists and engineers to manufacture energy devices from renewable and economical resources without environmental pollution. For excellent charge storage capacity, anode materials should be porous and have large surface area which can provide effective ion intercalation for electrochemical reaction. Carbon is a good conductor of electricity which can be used as a battery electrode. Different types of carbon material include are carbon nanotubes, carbon fibers, graphene and activated carbon are examples of EDLC materials. [8]

Charge storage mechanism includes pseudo capacitors and electric double layer Capacitors (EDLC). All the carbon materials such as graphene ,carbon nano tubes[6], carbon quantum dots and activated carbon shows EDLC behavior. Different synthesis mechanisms such as CVD, Arc Discharge, laser ablation, polymerization[11], graphite vaporization to nano diamond and wet chemical method could be used for the synthesis of porous activated carbon. These methods being expensive are mostly avoided.

2.3.1 Activated Carbon

Activated Carbon is one of the allotropes of carbon with an extra ordinary large internal surface area and pore volume. It is an amorphous solid with its structure best defined as a twisted network defective carbon layer plane, crosslinked by aliphatic bridging groups. These characteristics make it a good adsorptive material used in filtration, and liquid gas adsorption methods. [3]

2.3.2 Rice husk

Commercially activated carbon products can be produced from any carbonaceous material rich in carbon such as coal, wood, peat, nut shells etc. In recent years a wide interest is growing based on the production of activated carbon from natural agricultural waste and by products . The estimated annual global rice production is 570 million tons with 140 million tons of rice husk production[5]. The residues of rice husk create disposal problems though they are used as fuel for mill boilers, electricity generation and animal feed. A surplus amount gets wasted which creates a problem for mill owners. Some is readily burnt out and this contributes to environmental pollution.

2.3.3 Moisture and Ash Content

The porosity generated in activated carbon rises inversely to the ash content. More ash content less porosity will be generated as it will contain more silicon content.

The moisture and ash content of rice husk is measured according to the ASTM D2216-98 on oven drying the material at 110°C until a consistent weight is obtained[8], which shows it has 33% of ash content. By various acid and leaching process this presence of metallic impurities could be removed which is followed by various activation processes.

2.4 Activation methodologies

For the production of activated carbon, three types of activation processes were studied: physical activation, chemical activation, and hydrothermal carburization.

2.4.1 Physical activation

It is a four-step process. In the first stage, slow weight loss takes place during this carburizing process between 300K-470K depicting loss of moisture. Second stage represents formation of char structure through the evolution of gases and tars in the temperature range 470K to 770K. Third stage on the other hand, shows consolidation of char at a slower rate at temperatures between 770K to 1120K.

After this primary activation, the pores formed are clogged with disorganized carbon and because of this, pores are inaccessible, resulting in less surface area making it inept for high charge storage applications. This is where the second stage turns out to remove the clogging by treating it at higher temperatures between 1100K to 1250K to produce a structure with interconnected pores. This process is depicted in the figure below. [19]

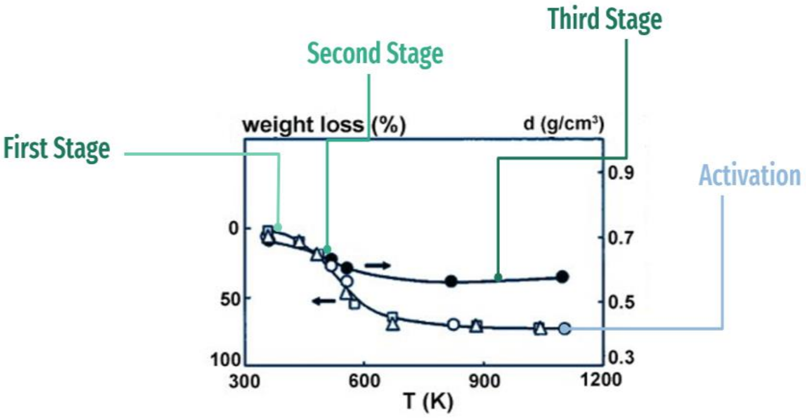


Figure 3: Physical Activation Process [19]

2.4.2 Hydrothermal Carburization

Inspired by nature's coal forming process, carburization takes place at lower temperatures and hence, requires a significant amount of time to develop porous carbon structure. The procedure takes place at temperatures less than 500K in a solution of water and at self-generated pressures. Due to its low cost and environmentally friendly process, it is considered as an alternative to physical and chemical activation.

This process can be divided into 4 stages: dehydration, polymerization, carbonization and use of reagents in the last step. First step of dehydration results in transition of carbohydrates to hydroxymethyl(furfurals). Second step is a polymerization process to convert furfurals to polyfurans. Afterwards, carbonization process takes place where intermolecular dehydration of polyfurans occurs. This is followed by use of KOH to enhance the properties of activated carbon in the fourth step.

Hydrothermal carburization activation results in a less developed structure of carbon, hence this method is generally used in conjunction with functionalization process or doping. In functionalization process, urea is used to form functional groups on the surface of activated carbon to enhance charge storage by N-H functional groups by bonding with the ions in the electrolyte. [19]

2.4.3 Chemical Activation

This is a single step process which makes use of a chemical precursor mixed with the carbon precursor and activated at an inert atmosphere at temperatures between 700K and 1200K. The main principle is the pyrolysis of the chemical precursor to decompose it and with higher temperatures during the ramp cycle, boil it to deposit the gaseous ions on top of the carbon precursor. At higher temperatures, the gaseous ions get intercalated in the carbon lattice to expand it and increase the surface area.

The main principle is the pyrolysis of the chemical precursor to decompose it and with higher temperatures, boil it to deposit the gaseous ions on top of the carbon precursor. At higher temperatures, the gaseous ions get intercalated in the carbon lattice to expand it and increase the surface area. [19]

2.5 Properties of electrodes

To help adopt a particular methodology, it is important to compare the characteristics of the obtained activated carbons from the methods discussed above and hence determine how that effects the electrochemical performance.

2.5.1 Carbon electrodes produced by physical activation

A reporting by Nabais et al. specifies activation of biomass by thermal activation in the presence of CO_2. Resulting activated carbon showcased a surface area of 1050 m^2 g^{-1} with a pore volume of 0.5 cm^3 g^{-1} and a specific capacitance of approximately 176 F g^{-1}. Taer et al. activated biomass into porous activated carbon monoliths with a highest BET surface area of 913 m^2 g^{-1} and a specific capacitance of 138 F g^{-1}.

Commonly implied method to produce activated carbon from biomass, this technique is considered inefficient as a lot of energy losses take place at high temperatures. Moreover, this process is time taking and non-environmentally friendly. [19]

2.5.2 Carbon electrodes produced by chemical activation

Chemically ACs usually exhibit high specific surface areas and well-defined micropore size distribution. Compared with physical activation, chemical activation has several superior merits, such as lower conversion temperature, shorter activation time, higher carbon yield, larger specific surface area and higher porosity.

KOH is the frequently used activating agent at higher temperatures and because of this, also exhibits well defined pore size distribution, super-high specific surface area (up to 3000 m^2 g^{-1}), pore volume up to 2.28 cm^3 g^{-1} and specific capacitance up to 421 F g^{-1}.

However, the use of salts like KOH, KCl and $ZnCl_2$ are detrimental to equipment, causes corrosion over a span of time and consumes huge amount of energy due to activation at temperatures up to 1300°C. Hence, as an alternative, other precursors can be used to activate carbon precursor by facilitating activation at consequently temperatures below the conventional values and hence, avoid corrosion. [19]

2.5.3 Carbon electrodes from hydrothermal carburization

Upon multiple modifications of this process, which includes functionalization and usage of chemical reagents for activation, high BET surface areas of ~2200 $m^2 g^{-1}$, high specific capacitance of up to 200 F g^{-1} can be obtained.

However, as compared to activated carbons, the hydrothermally carburized carbonaceous materials exhibit less pores and low specific surface area, which is not desirable for the applications such as catalysis, adsorption, or energy storage, in which controlled porosity at the nanometer scale is preferred. [19]

2.6 Adopted activation mechanism

To obtain the best of the above discussed processes, it is apt to use two processes in conjunction or in a hybrid to maximize the surface area by utilizing less energy, in a way which is more environmentally friendly and less time consuming.

2.6.1 Hybrid Methodology

For this, a wide variety of chemical precursors were studied and for our course of action, it was decided to use trisodium phosphate dodecahydrate, potassium bicarbonate and urea for activation and functionalization.

Trisodium phosphate will help provide gaseous sodium ions for activation at 100^0C. Other than that, due to its dodecahydrate structure, it will provide localized steam to help unclog pores formed during activation, giving it a characteristic of physical activation. Steam may be important for unclogging pores but a high amount of moisture can form a hydro char instead of hard activated carbon which can be avoided by drying the mixture in a conventional oven and vacuum oven prior to heat treatment. Potassium bicarbonate on the other hand, boils at 333^0C to provide gaseous potassium ions which are responsible for activation at higher temperatures. The activation is therefore hybrid comprising of physical and chemical characteristics.

In addition to this, urea would be utilized to help with the functionalization process by formation of amine group on the surface to enhance charge adherence by bonding with ions in the electrolyte.

2.6.2 Heat treatment

In our strategy, heat treatment temperatures were optimized to relatively very low degrees i.e. 600, 700 and 800 degrees Celsius. As low boiling point possessing salts were utilized, various soaking temperature were employed in heating cycle corresponding to boiling point of each salt and urea. Trisodium phosphate dodecahydrate boils at 100^0C while urea and potassium bicarbonate boils at 200^0C and 400^0C.

The gaseous sodium and potassium ions which are deposited on rice husk after boiling are responsible for the activation process. These ions diffuse and impregnate the carbon lattice at temperatures in range 600^0C-800^0C. Resultantly, the carbon lattice expands because of this intercalation and surface area increases consequently. Urea on the other hand boils and functionalizes the surface and hence, enhance charge storage.

CHAPTER 3

METHODOLOGY

3.1 Acquiring Raw materials

Rice husk was obtained for free from the local market of Samundri in Punjab, Pakistan while multiple coal samples were obtained from Thar and Sondha regions of Sindh, Pakistan.

3.2 Pre-processing of raw materials

Before loading the mixture in the porcelain boats, the rice husk has to be cleaned and removed of impurities like dust, metallic impurities and silica. The mixture is then dried to eradicate it from moisture and loaded into porcelain boat, followed by quartz tube in tube furnace for activation process.

3.2.1 Washing and Drying

As obtained bio waste (rice husk) samples were weighed and washed in a 3-step process. Firstly, it was washed with a 400ml, 6mol/liter solution of hydrochloric acid in a fume hood for 6 hours through magnetic stirrer. The acid was then drained and the rice husk was then washed with 400ml, 10% hydrofluoric acid in a fume hood overnight to remove silica. Finally, the acid was drained and the rice husk was then ultrasonicated with DI water to remove the traces of acid. Drying process was carried out overnight in conventional and vacuum oven at 70^{0}C. Washing and drying steps are elaborated in Figure 4. [4]

Figure 4: Elaboration of various steps involved in washing of the as obtained rice husk samples.

3.2.2 Mixing with Salts

For ion impregnation and later activation, cleaned and washed rice husk samples (1.00g in each experiment) were mixed with an optimized weight ratios of potassium bicarbonate (0.475g) + trisodium phosphate dodecahydrate (0.232g) + Urea (0.50g). Potassium bicarbonate and trisodium phosphate dodecahydrate will provide gaseous sodium and potassium that will intercalate in the carbon lattice to expand it and increase its surface area. Other than that, urea is being used for the functionalization of the surface to enhance charge storage through chemical bonding of N-H group with the Na^+ and K^+ ion during the heat treatment cycle.

Table 3-1 Preparation of six samples with required number of reagents and soaking time

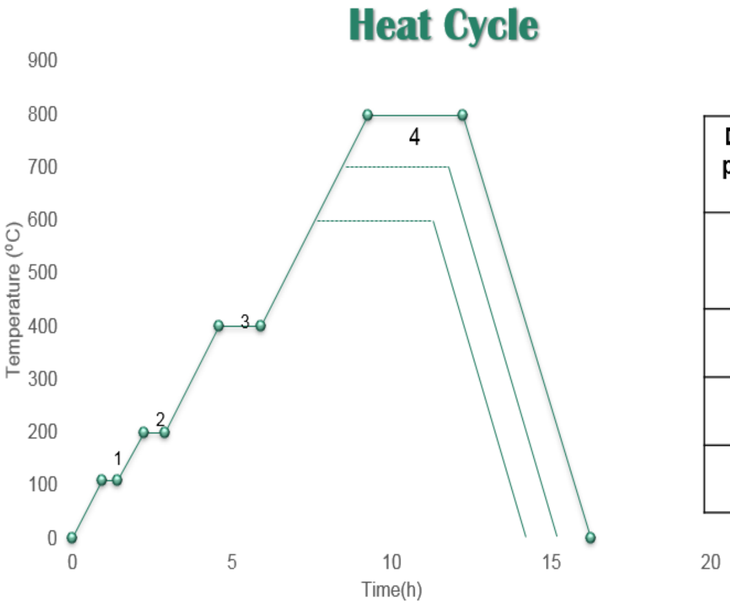
Sample no.	Temp of tube furnace(˚C)	Activation Reagents (g)	Activation Soaking Time (hours)
1	600	$KHCO_3$(0.475)+$Na_3PO_4.H_2O$(0.232)+Urea(0.50)	3
2	700	$KHCO_3$(0.475)+$Na_3PO_4.H_2O$(0.232)+Urea(0.50)	3
3	800	$KHCO_3$(0.475)+$Na_3PO_4.H_2O$(0.232)+Urea(0.50)	3
4	600	$KHCO_3$(0.475)+$Na_3PO_4.H_2O$(0.232)+Urea(0.50)	4
5	700	$KHCO_3$(0.475)+$Na_3PO_4.H_2O$(0.232)+Urea(0.50)	4
6	800	$KHCO_3$(0.475)+$Na_3PO_4.H_2O$(0.232)+Urea(0.50)	4

3.2.3 Drying

The mixture was then dried in a conventional oven at 70^0C for 12 hours, followed by drying in a vacuum oven at 70^0C for 12 hours. The mixture in porcelain boat was sealed through aluminum foil and transported to tube furnace for activation.

3.3 Tube furnace

In our strategy, heat treatment temperatures were optimized to relatively very low degrees i.e. 600, 700 and 800 degrees Celsius. Before setting the cycle, sample was loaded into porcelain boat and into quartz tube within the tube furnace. Next, vacuum was generated through the rotary pump and purging was performed to avoid contamination by adsorbed gases. Sample was then kept in inert atmosphere. Complete depiction of the heat cycle is given in the Figure 5. As low boiling point possessing salts were utilized, various soaking temperature were employed in heating cycle corresponding to boiling point of each salt and urea. Trisodium phosphate dodecahydrate boils at 100°C and hence, the mixture was soaked at 110°C for 30 minutes. Consequently, urea and potassium bicarbonate were boiled at 200°C and 400°C and soaked at this temperature for 50 and 80 minutes respectively according to the quantity of the salt in the mixture. Ramp rate of this heat cycle was kept at 2.5°C/min to ensure slow and gradual activation of the carbon precursor, i.e. rice husk. Final activation was carried out at temperatures ranging from 600°C-800°C followed by furnace cooling sample.



Data point	Soaking Time (min)	Purpose
1	30	Boiling of Na_3PO_4 $12H_2O$
2	50	Boiling of $CO(NH_2)_2$
3	80	Boiling of $KHCO_3$
4	180	Activation

Figure 5: Illustration of various steps involved in heat treatments of the bio waste samples mixed with low boiling salts.

3.3.1 Activation during heat cycle

The gaseous sodium and potassium ions which were deposited on rice husk after boiling at 110°C and 400°C are responsible for the activation process. These ions diffuse and impregnate the carbon lattice at temperatures in range 600°C-800°C.

Resultantly, the carbon lattice expands as a result of this intercalation and surface area increases consequently. Urea on the other hand, is responsible for functionalization of the surface by forming N-H bonds which will attach.

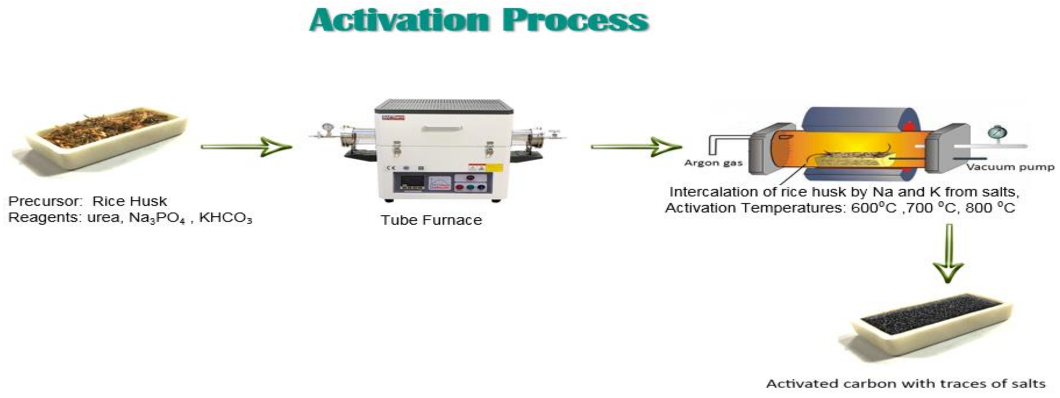


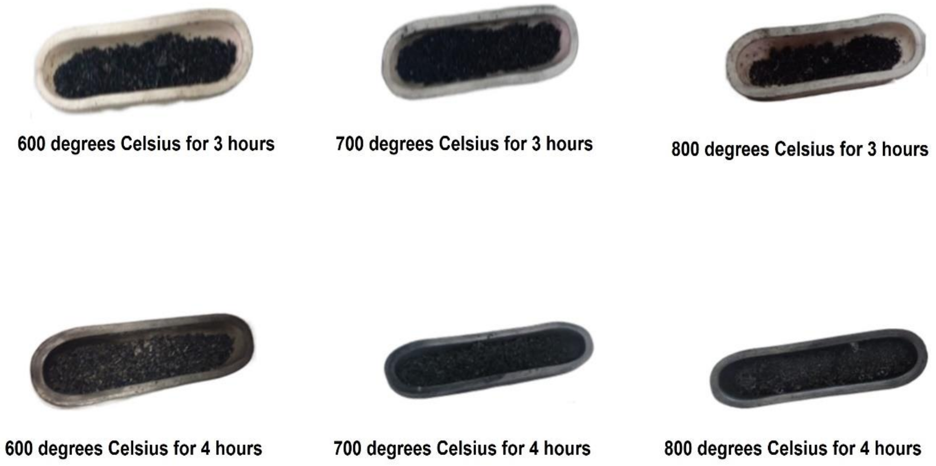
Figure 6: Complete schematic illustration of the bio waste to activated carbon conversion process.

3.4 Post-processing

The sample is then post-processed to obtain activated carbon with minimal traces of salt.

3.4.1 Washing

After heat treatment, samples were thoroughly washed with de ionized water and ethanol to get rid of the macro residues of salts. With the increasing temperature and soaking time for activation, the samples got visibly blacker and had less traces of salt that could be seen by naked eye. Digital images of differently treated samples are collaged in Figure 7.


600 degrees Celsius for 3 hours **700 degrees Celsius for 3 hours** **800 degrees Celsius for 3 hours**

600 degrees Celsius for 4 hours **700 degrees Celsius for 4 hours** **800 degrees Celsius for 4 hours**

Figure 7: Digital images of differently treated samples.

3.4.2 Centrifuge and Drying

After balancing the mass of each tube comprising of DI water and activated carbon, the tubes are centrifuged at 4000 rpm for 2-3 hours. Resultantly, the less dense activated carbon settles at the bottom of the tube that can be scraped off after draining out the water.

The obtained sample is then dried overnight in a conventional oven at 70^0C and then crushed in a mortar pestle. Afterwards, the sample is weighed to calculate the yield obtained. Multiple samples were prepared following the same process parameters and the average yield was calculated to be approximately 41%.

3.5 Coin Cell Assembly

The prepared anode material is then assembled in a coin-cell and tested for electrochemical performance.

3.5.1 Electrode formation by tape casting

First of all, activated carbon is mixed with binder and carbon black in fixed ratio and dissolved in N-methyl-2-pyrrolidone (NMP) solvent to form slurry with an appropriate viscosity. The table below illustrates the information given above.[16]

Table 3-5: Percentage Ratio of binders vs sample

Activated Carbon	70%
Polyvinyldeneflouride as binder	15%
Carbon Black	15%

Copper foil and stainless steel is then thoroughly cleaned with ethanol and taped onto a glass to keep it in place as shown in Figure 8 and 9 respectively. The slurry in then poured onto the foil and then evenly spread out with the help of a blade.

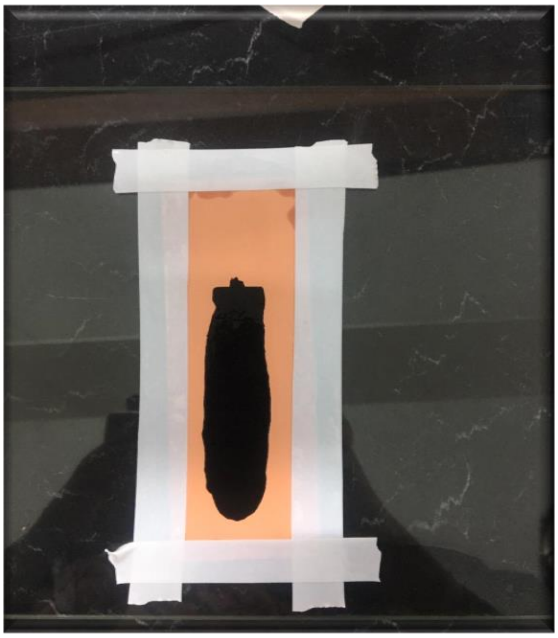


Figure 8: Coin cell preparation using copper foil

Figure 9: Coin cell preparation using stainless steel

3.5.2 Vacuum Drying and Electrode Cutting

The copper foil and stainless steel is then detached from the glass and placed in an enveloped aluminum foil to be dried in a vacuum oven at 60^0C for 12 hours.

The obtained electrode and zinc metal are then cut in a 12mm diameter as shown in figure below.

Figure 10: Electrode cutter

3.5.3 Assembly of half cell

The components of the half-cell, i.e. positive casing, negative casing, spacer, separator, spring, anode and cathode were then assembled to form a half cell as shown in Figure 11. Orderly, a spring and spacer is placed on top of positive case with a help of tweezer, followed by zinc metal, separator, hard carbon anode, spacer and finally the negative casing. Other than that, spacer helps give backing to the soft metal and spring helps keep the half-cell pressed together. Separator on the other hand is soaked with zinc sulphate solution, i.e. electrolyte. [16]

The electrode with copper foil backing is sent abroad to test for sodium sulfur batteries due to unavailability of glove box here while the electrode with stainless steel backing is tested for zinc ion battery.

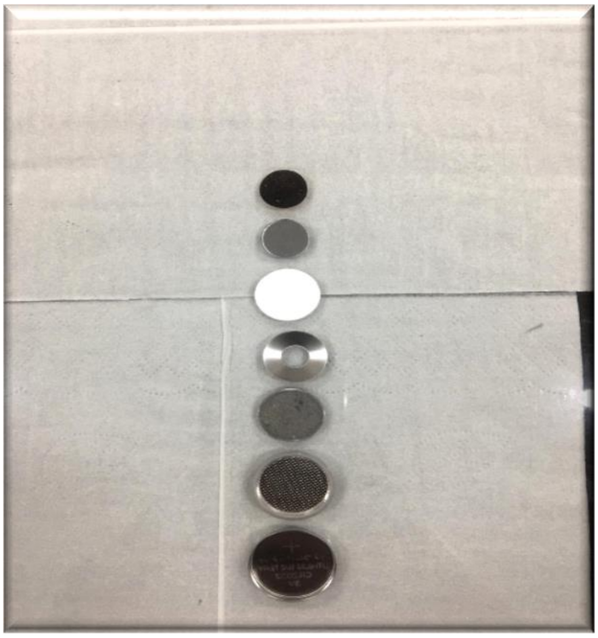


Figure 11: Coil cell assembly

The half-cell is then punched at 700 psi to keep it intact and later on to be used for electrochemical testing and lighting up an LED bulb. Finally, two half cells of 1.5V each are used to light up a red LED that operates at 2.5V as shown in figure 11 below.

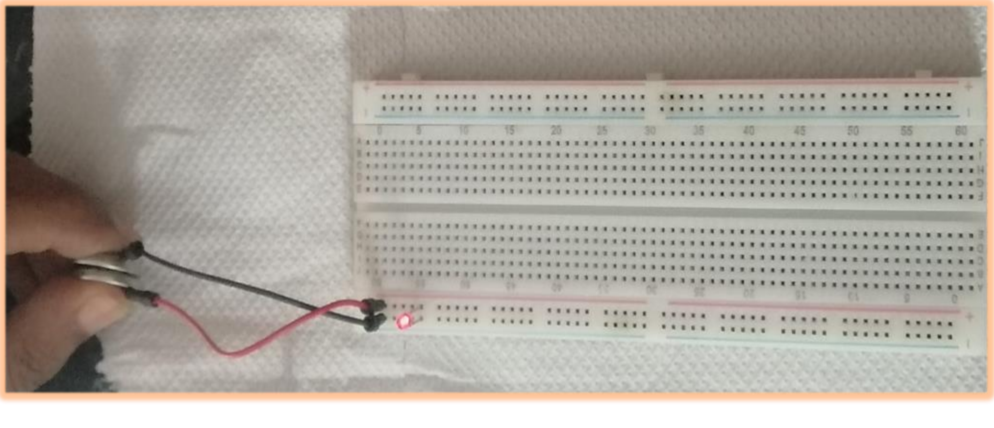


Figure 12: LED bulb lit by Zn metal half-cell using activated carbon cathode

CHAPTER 4

TESTING AND RESULTS

4.1 Characterizations

Activated carbons have played important role as electrode materials in order to make EDLCs (Electric double layer capacitors) due their large surface areas, excellent electrochemical performance, good electrical conductivities and chemical resistance.[7]

In order to ensure complete conversion of rice husk to porous activated carbon, several techniques were applied on attained samples. These techniques include Scanning Electron Microscopy, X-ray diffraction, Fourier transform infrared microscopy, Raman spectroscopy and Brunauer-Emmet-Teller (BET).

XRD confirmed different phases of carbon present in the obtained sample whereas SEM showed presence of pores in differently treated sample. The revealed morphological features helped distinguish the results of differently treated samples. Degree of graphitization was observed by analyzing obtained Raman spectroscopy and BET was used to determine pore size, distribution and surface area of samples.

4.1.1 XRD analysis

XRD analysis shows diffraction peaks at same angles, however with increment of activation temperature, the width of the peak narrows down showing change in degree of graphitization with the highest temperature having a more developed crystal.

As per figure 12 shows (treated by soaking for 3 hours), clear peaks corresponding to carbon can be seen in each of the samples treated at 600^0C, 700^0C and 800^0C. Moreover, this peak gets more intense and sharper as the temperature is raised from 600^0C to 800^0C. However due to insufficient washing of initial samples prepared, peaks of remaining salts can also be seen.

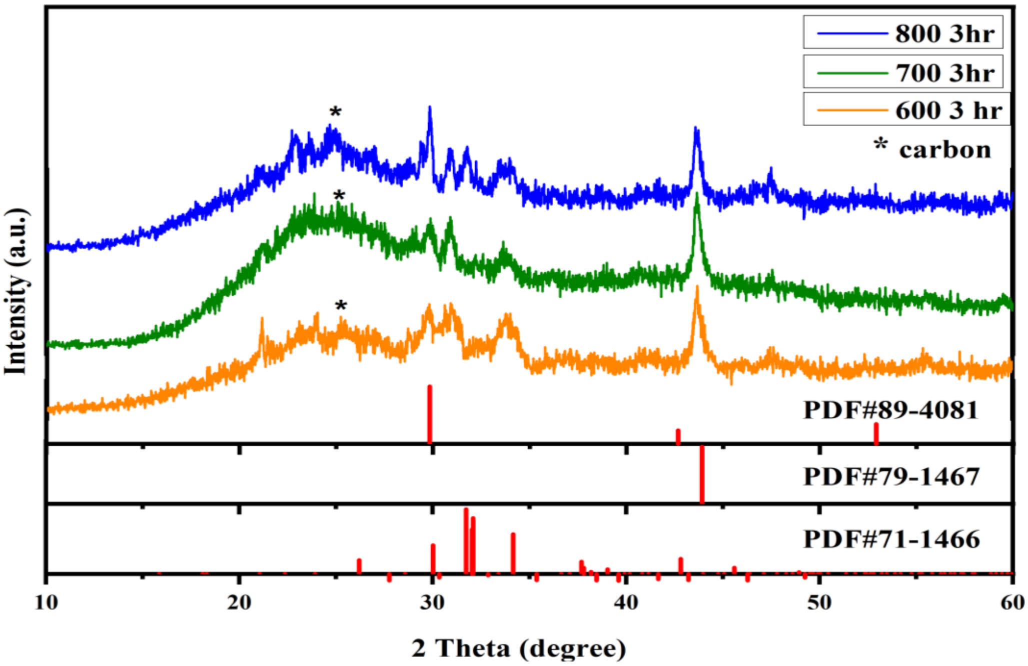


Figure 13: XRD plot for sample activated for 3 hours

Figure 13 shows results for samples treated by soaking for 4 hours with same temperatures as above. The sample treated at 800^0C and soaked for 4 hours shows sharpest and most intense peak for carbon developed.

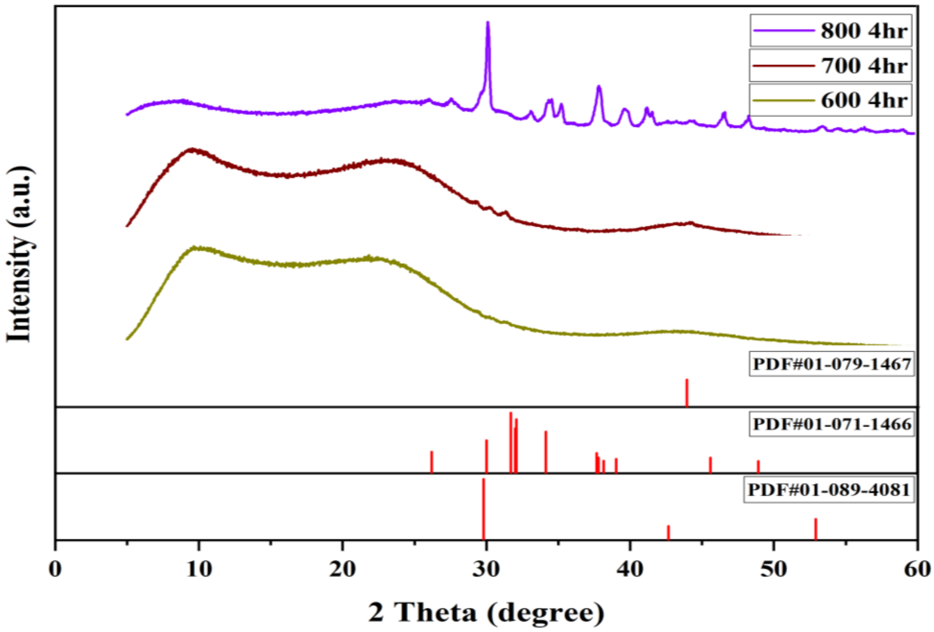


Figure 14: XRD plot for sample activated for 4 hours

4.1.2 Raman Analysis:

To identify the nature of developed carbon, Raman analysis is carried out. The Raman confirm the microstructural changes that took place during the activation of the samples which varies as per the temperature changes. [7]

In our application, we need as much disordered carbon as possible. The characteristic peaks at around 1310cm^{-1} and 1610cm^{-1} in figure 16 represent the D and G bands. D band is associated with the disordered structure whereas the G band is associated with the ordered layered graphitic structure. The ratio of these two bands, I_G/I_D, is used to estimate the degree of graphitization. These results indicate that the higher activation temperature increase the degree of graphitization, confirming our observations from the XRD data. [8]

As seen in figure 14, at soaking time for 3 hours and 4 hours, peak positions of D and G bands for samples treated at 600^{0}C, 700^{0}C and 800^{0}C, are same however the ratio of intensities of D and G bands can be seen to increase as the temperature increases. This ratio is related to structural defects caused by heteroatom doping. Hence, it can be concluded that the doping became facile at higher temperatures and carbon is easily activated.

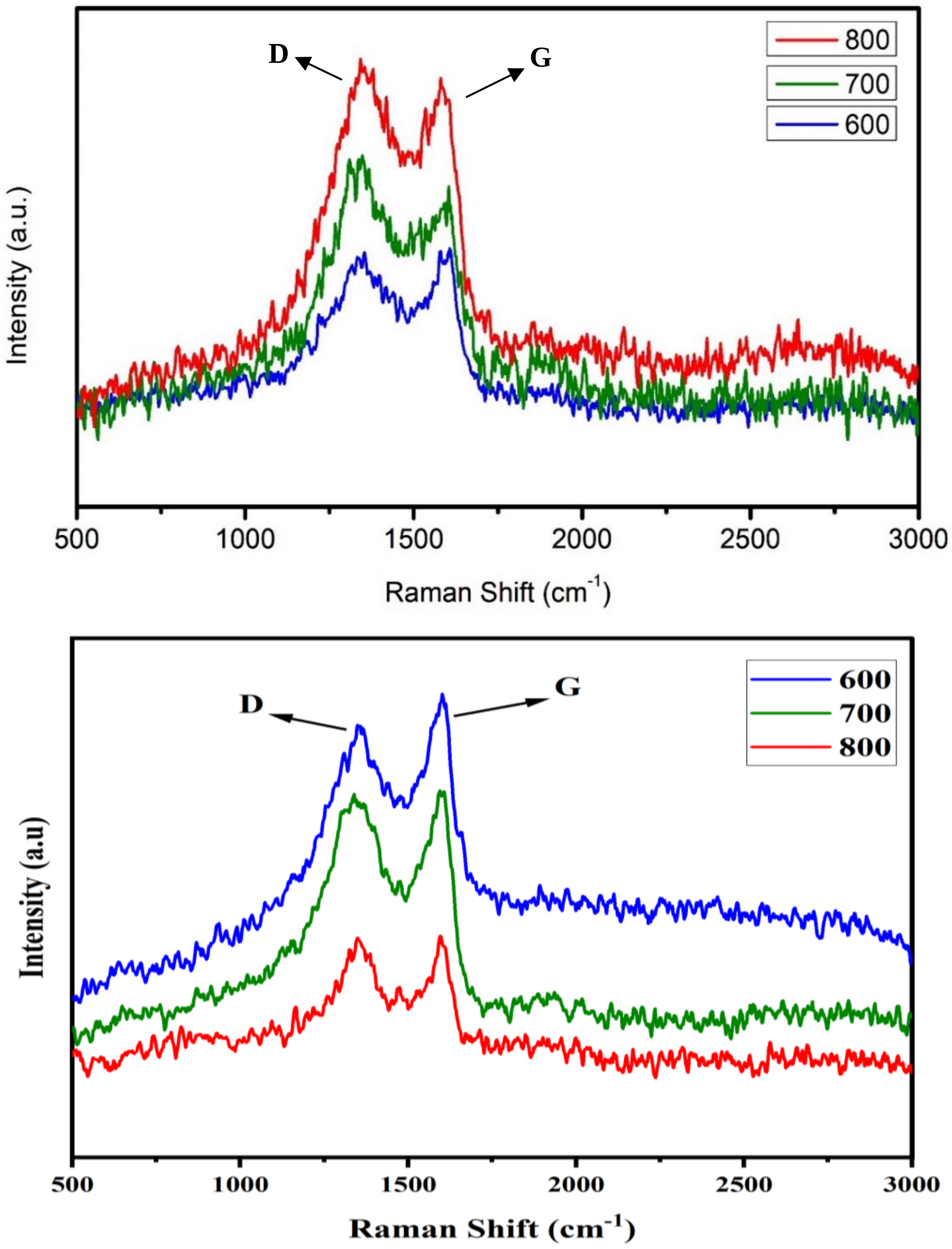


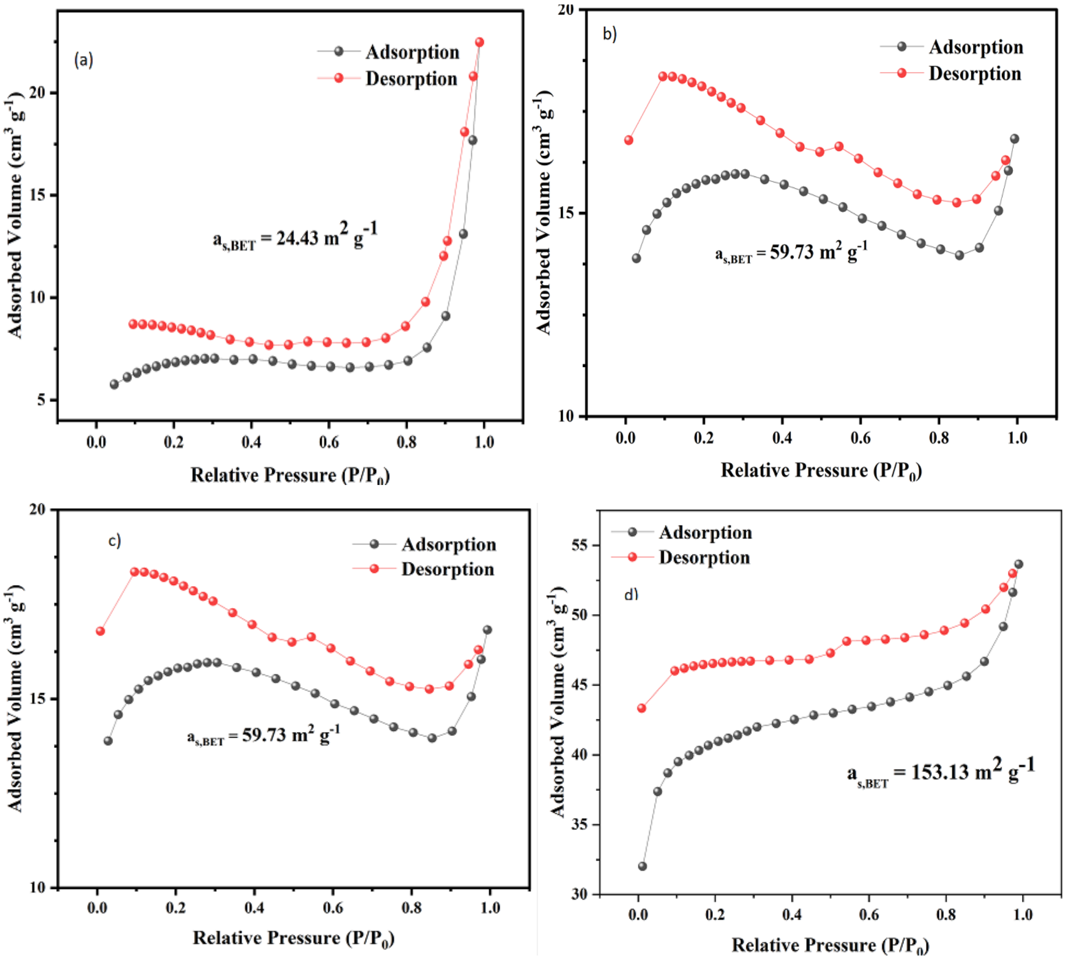
Figure 15: Raman Plots for samples activated at 3 hours and 4 hours

4.1.3 BET Results

This technique is applied to check the surface area, volume, pore density and pore distribution of the activated porous carbon however, in this application, surface area is the parameter of our concern. Maximum surface is desired for maximum value of specific capacitance of the battery obtained as greater surface area and pore volume facilitate intercalation of more sodium ions. [17]

The obtained data from BET was transferred to Origin software and the axes were as set as relative pressure against absorbed volume to obtain the plots shown in figure 15.

As seen from the results of BET in figure 15, maximum surface area was obtained for samples under conditions of 700^{0}C temperature and a soaking period of 4 hours referring to figure 4(e), making this the optimum condition for making activated carbon with high surface area maximising the intercalation process.



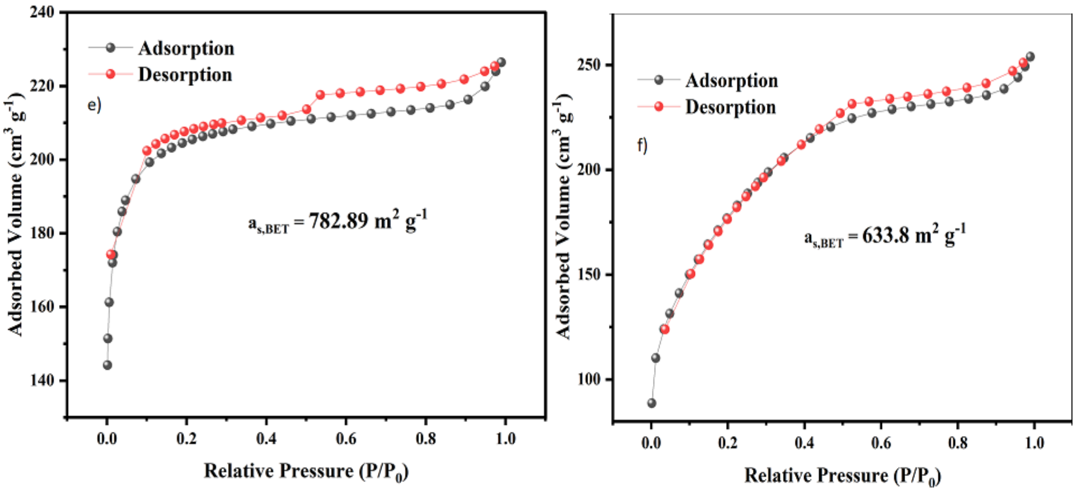


Figure 16: BET plots samples treated at different conditions

(a) 600^{0}C, 3hours (b) 700^{0}C, 3hours (c) 800^{0}C, 3hours

(d) 600^{0}C, 4hours (e) 700^{0}C, 4hours (f) 800^{0}C, 4hours

4.1.4 FTIR analysis:

Any functional groups present in the activated carbon attained from rice husk are characterised using FTIR shown in figure 16 and 17. Again, three different peaks were obtained for three different samples, each treated at 600^{0}C , 700^{0}C and 800^{0}C. As the temperature of activation was raised, more absorbance was observed indicating presence of more number of functional groups in activated carbon. The most wide and visible peak was obtained at 3535.5cm^{-1} corresponding to the –OH group justifying good sufficient activation whereas all samples showed peaks at 3535, 2080, 1635, 1399, 1109, and 792 cm^{-1}.Another peak centered at 1635cm^{-1} was obtained indicating presence of C=C bond.

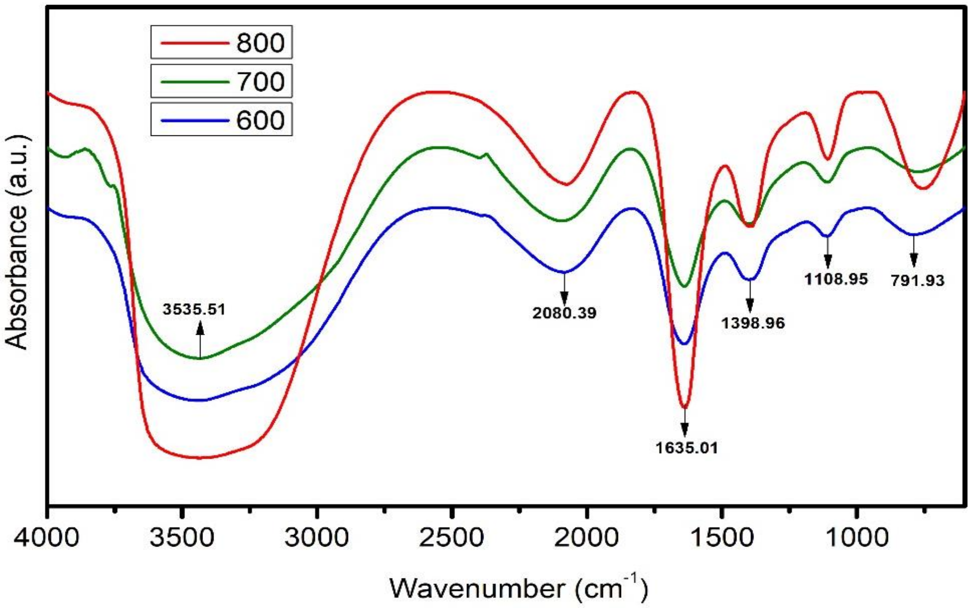


Figure 17: FTIR plot for samples activated for 3 hours

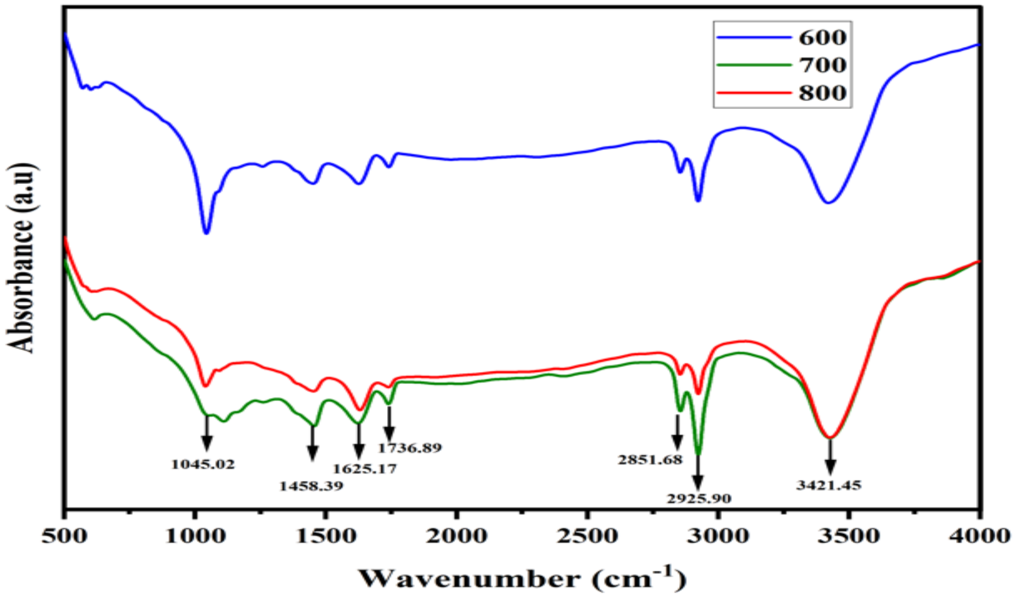
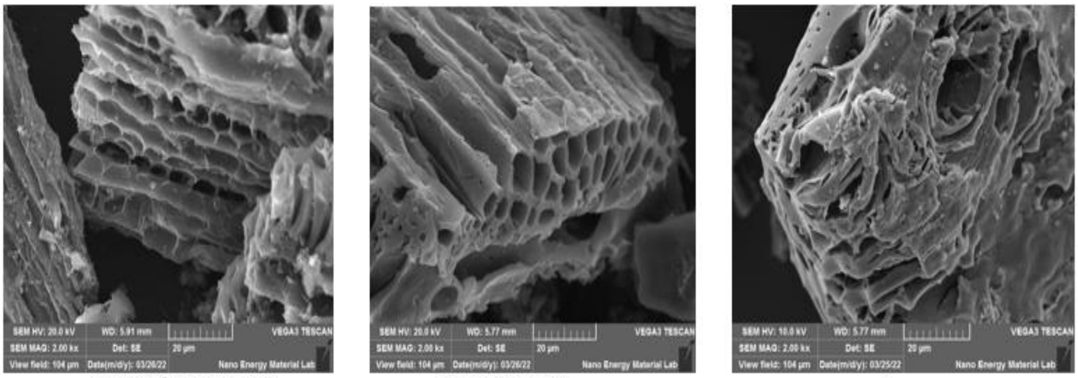


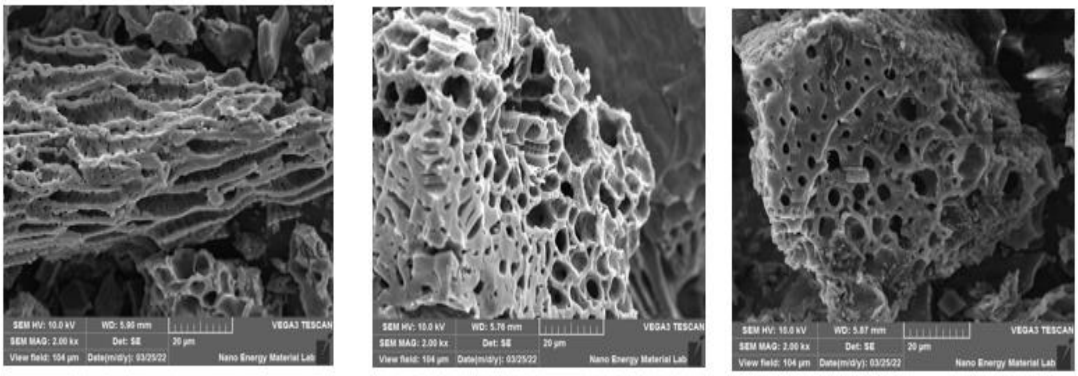
Figure 18: FTIR plot for samples activated for 4 hours

4.1.5 Scanning Electron Microscopy:

The surfaces of the activated carbon were observed using SEM. Images attached below taken at a magnification of 2.00kx, confirm presence of high level of porosity in the activated carbon attained from rice husk. Samples treated at higher temperatures of 700^0C and 800^0C show higher degree of porosity and well-developed pores. Another parameter that was altered is the soaking period which was changed from three to four hours showing an increase in porosity upon prolonged duration.



(a) 600°C, 3 hours (b) 700°C, 3 hours (c) 800°C, 3 hours



(d) 600°C, 4 hours (e) 700°C, 4 hours (f) 800°C, 4 hours

Figure 19: SEM images for activated carbon

4.2 Electrochemical Testing

The electrochemical performance was checked by placing the activated carbon electrode in a half-cell setup with zinc as cathode, activated carbon as anode and zinc sulfate as the electrolyte. The electrochemical performances of the activated carbon electrodes were investigated by CV and Galvano static charge discharge tests using zinc half-cell.

4.2.1 Cyclic Voltammetry:

In a cyclic voltammetry test, graph is plotted between two potentials with voltage and current on x and y axes respectively. Graph is plotted by scanning at a constant rate for a fixed number of cycles. For every cyclic voltammogram plotted, the upper curves represent oxidation while the lower curve represents reduction, Hence, the redox processes of activated carbon were investigated through CV plots. [3]

Method:

To obtain the CV plots, we connected the prepared coin cell with activated carbon as anode and zinc as cathode, to the battery testing equipment using clips. The red terminal connected to the positive whereas the black terminal connected to the negative electrode of the cell.

The Beware battery tester's BTS client 8.0 software was used to plot these results in which the parameters such as number of sweep cycles, scanning rate and potential windows are set.

Results:

The obtained voltammogram of zinc half-cell setup is attached below is for the cell made from sample treated at 700^0C and soaked for 4 hours. All plots obtained at the scan rates from $2mVs^{-1}$ to $100mVs^{-1}$ have shown near rectangular shapes confirming the EDLC (electric double layer capacitance) behavior of activated carbon electrode. Moreover, the rectangular area increased without deformation as the scan rate was increased to $100mVs^1$ showing excellent rate performance.

Specific capacitance can also be calculated using the area under the graph of these plots however, the values are not very accurate thus GCD (galvanostatic charge discharge) was performed later.

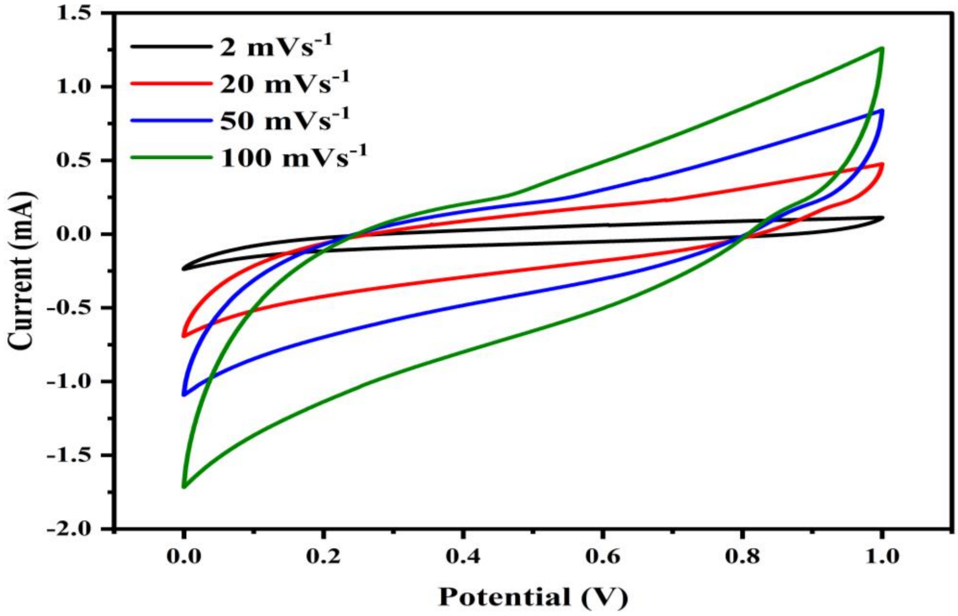


Figure 20: CV plot of zinc half-cell

4.2.2 Charge discharge cycling:

For a fixed number of cycles, battery is tested by charging and discharging hence it is real time testing. A fixed positive current value is applied during charging while a negative current value applied during discharge. Hence, an operation voltage profile of the battery is made. When different current rates were applied ranging from 0.1Ag^{-1} to 1.5Ag^{-1}.

Method:

The cell was connected to the battery testing setup at a specific channel. Beware battery tester's BTS client 8.0 software was used to plot these results. Then the specific parameters for running the test were set with different current rates. Both upper and lower bound of the battery operating voltage are defined. Once the required number of cycles have, the number of iterations repeat and setup the process again.

The obtained data is transferred to an excel sheet and this is then plotted on Origin software which plots specific capacity against the voltage. [3]

Results:

When different current rates were applied ranging from 0.1Ag^{-1} to 1.5Ag^{-1}, visible changes in plots for discharging are observed rather than those charging however the obtained specific capacitance decreases.

As the graphs flattens during the discharging phase, zinc ion storage takes place in the activated carbon anode at an approximate potential range of 0.8V to 1.0V. Maximum specific capacitance of 160mAhg^{-1} After this range, slopes of the graphs vary with increasing current rates, this is because of minimization of diffusion as ions accumulate at anode. Hence, penetration of these ions also decreases into anode resulting in the decrease of overall specific capacitance of the half-cell.

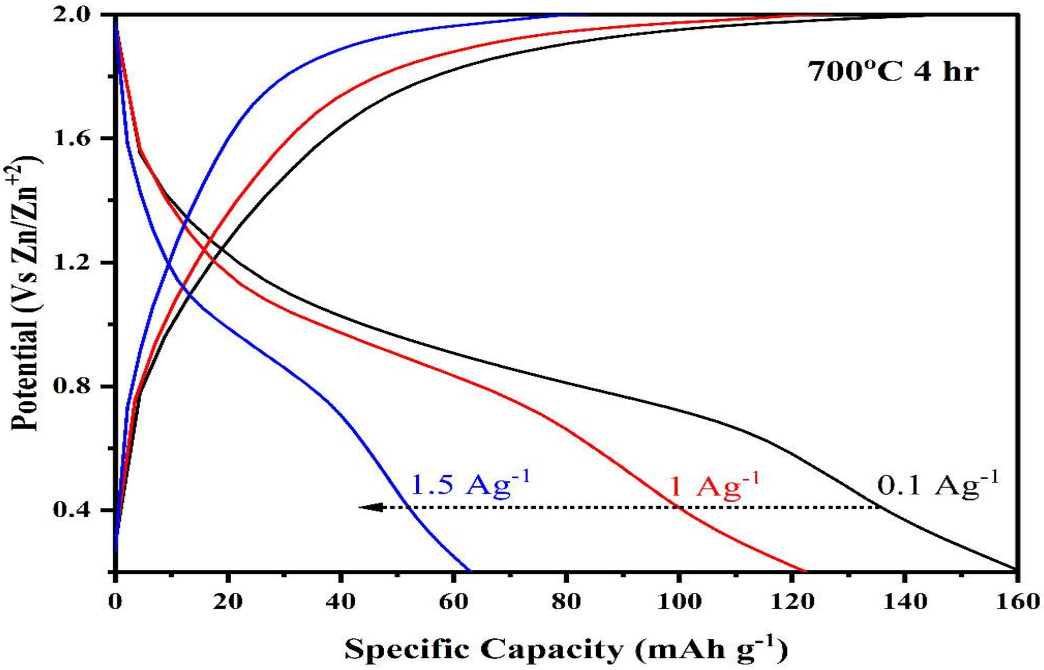


Figure 21: GCD plot of zinc half-cell

CONCLUSIONS

The chosen hybrid methodology has proven to give a maximum surface area of 782.89m^2 g^{-1} of activated carbon which is sufficient to facilitate the intercalation of sodium ions during charging cycles.

The prepared zinc ion half-cells have shown sufficient specific capacitance of 160mAhg^{-1} as determined through the GCD results and linked software. Moreover, CV analysis has indicated EDLC behavior of activated carbon anode.

However, assemblage of activated carbon anode in sodium sulfur battery could not be done due to unavailability of glove box at the campus. Results however give indication that if, activated carbon electrodes are further used in sodium sulfur batteries, they can give highly favorable results with high energy density, high energy capacity and most importantly through an economical and sustainable route.

Further testing of activated carbon as anode of sodium sulfur batteries would be performed at Institute of Nano-sensors Hanyang University, Ansan, South Korea.

REFERENCES

[1] Abdul Raheem, S. A. (2016). Renewable energy deployment to combat energy crises in Pakistan . *Energy sustainable and society* , 13.

[2] Adelhelm, P., Hartmann, P., Busche, M., & Janek, J. (2015). From lithium to sodium: cell chemistry of room temperature sodium air and sodium sulphur batteries. *Journal Of Nanotechnology*, 1016-1055.

[3] Baker, F. S., Miller, C. E., & J, A. (2000). Activated Carbon. *Chemical Technology*.

[4] E. Menya, P. O. (2017). Production and performance of activated carbon from rice husks for removal of natural organic matter from water: A review. *Chemical Engineering Research and Design*.

[5] Kalderis, D., Bethanis , S., & Paraskeva, P. (2008). Production of activated carbon from bagasse and rice husk by single chemical activation method at low retention time. *Bioresource technolgy*(99), 6908-6916.

[6] Li, X., Cai, W., Kim, S., & Piner, R. (2009). Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science, 324*(5932).

[7] liou, T. H., & Wu, J. S. (2009). Characteristics of microporous/mesoporous carbons prepared from rice husk under base and acid treated conditions . *Journal Of Hazardous Materials* , 693-703.

[8] Mondal, M., & Goswami, D. K. (2021). Lignocellulose based Bio-waste Materials derived Activated Porous Carbon as superior electrode materials for High performance Super capacitors. *Journal Of Energy Storage* .

[9] Muhammad Assad Munawar, A. H. (2021). Challenges and opportunities in biomass ash management and its. *Renewable And Sustainable Energy Reviews* , 30.

[10] Oswal, M., Paul, j., & Zhao, R. (2010). *A comparitive study Of Lithium Ion Batteries.* Southern California.

[11] Reddy, K. R., Sin, B. C., & Ryu, K. S. (2009). In situ self-organization of carbon black–polyaniline composites from nanospheres to nanorods: Synthesis, morphology, structure and electrical conductivity. *Synthetic Metals, 159*(19=20), 1934-1939.

[12] Riaz Uddin, H. R. (2021). Energy Storage for Energy Security and Reliability through Renewable Energy technologies: A new Paradigm for energy policies in turkey and Pakistan. *sustainaability* , 17.

[13] Soleimani, M., & Kaghaschi, T. (2007). Agricultural Waste Conversion to Activated Carbon By Chemical Activation with Phosphoric Acid . (5), 649-654.

[14] Waag, W., Fleischer, C., & Sauer, D. U. (2014). Critical review of the methods for monitoring of lithium-ion batteries in electric and hybrid vehicles. *journal Of power Sources, 258*, 321-339.

[15] Wang, L., Hustad, J. E., & Skjevrak, G. (2012). A critical review on additives to reduce ash related operation problems in biomass combustion. *Energy Procedia*, 20-29.

[16] Xinpei Ma, J. W. (2019). Aqueous V2O5/activated carbon zinc-ion hybrid capacitors with high. *Journal of Materials Science: Materials in Electronics*.

[17] Yu, K., Li, J., Qi, H., & Liang, C. (2018). High-capacity activated carbon anode material for lithium-ion batteries prepared from rice usk by a facile method. *Diamond and Related Materials* , 139-145.

[18] Yu, X., & Manthiram, A. (2016). erformance Enhancement and Mechanistic Studies of RoomTemperature Sodium−Sulfur Batteries with a Carbon-Coated. *Chemistry Of materials* , 896-905.

[19] Zan Gao, Y. Z. (2016). Biomass-derived renewable carbon materials for electrochemical energy storage. *Material Research Letters*.