

Pyrolysis reactions of suitable natural precursors towards Synthesis of Carbon Electrode materials for Energy Storage



Thesis submitted towards the partial fulfilment of BS-MS Dual degree

By

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Under the guidance of

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To

The Department of Chemistry

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH

PUNE

DEDICATED TO MY BELOVED PARENTS....

CERTIFICATE

This is to certify that this dissertation entitled “**Pyrolysis reactions of suitable natural precursors towards Synthesis of Carbon Electrode materials for Energy Storage**” submitted towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune; represents original research carried out by **Golu Parte** at National Chemical Laboratory (NCL) under the supervision of **Dr. Satishchandra B. Ogale**, Scientist, CSIR-National Chemical Laboratory, Pune; during the academic year 2014-2015.



Dr. Satishchandra B Ogale

(Supervisor)

Date: 29/04/2015

Place: Pune

DECLARATION

I hereby declare that the matter embodied in the thesis entitled “**Pyrolysis reactions of suitable natural precursors towards Synthesis of Carbon Electrode materials for Energy Storage**” are the result of investigation carried out by me at the Department of Physical and Material Chemistry, National Chemical Laboratory, Pune, under the guidance of Dr. Satishchandra B Ogale and same has not been submitted elsewhere for any other degree.

Place: Pune

Date: 13/04/2015



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–Golu Parte

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List of Abbreviations

0D	Zero Dimensional
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
BET	Brunauer Emmett Teller
C_s	Specific capacitance
CNT	Carbon Nanotube
CV	Cyclic Voltammetry
D. I.	De Ionized
EDL	Electric Double Layer
EDLC	Electrochemical Double Layer Capacitor
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent series resistance
FESEM	Field Emission Scanning Electron Microscope
FWHM	Full Width at Half Maximum
HRTEM	High Resolution Transmission Electron Microscope
LIB	Lithium Ion Battery
PVDF	polyvinylidene difluoride
SEI	Solid Electrolyte Interphase
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope

XRD

X-ray Diffraction

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➤ **ABSTRACT**

Clean energy is perhaps the most critical demand of today's developing world, arising out of rapid exploitation of non-renewable sources of energy. Therefore, we are compelled to look for solutions in the form of renewable sources of energy. Since the time domain for harvesting renewable sources of energy does not coincide with our practical usage, we need efficient energy storage systems. Among various energy storage systems, electrical storage systems are most important. These include batteries and Supercapacitors. In particular, for electrical double layer type Supercapacitors high surface area, porous and highly conducting carbon is highly desirable. Also, it must be derived from low cost precursors by simple protocols.

In this research, suitably controlled pyrolysis of unexplored biomass and bi-wastes such as yogurt, biogels like pectin, alginate and agarose prove to be a novel and easily scalable precursors for supercapacitor carbon.

Here I report synthesis of carbon from natural gel, pectin, as a precursor by suitably controlled pyrolysis. The carbon synthesized from pectin offers a high capacitance of 310 F/g at current density of 1A/g in aqueous medium.

1. INTRODUCTION

1.1 Nanomaterials and Energy

Materials have played a vital role in shaping the human civilization and their evolution.¹ Nano materials have potential applications in different fields, Because of their unique magnetic, optical, electrical properties. These properties make nano materials promising in electronics, medicine and other fields. Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanoscience deals with materials with at least one external dimension being smaller than 100 nm. The nanoscience is manipulating the material at atomic, molecular and molecular level, at these level properties differ from the larger scale. Nanotechnology is considered as emerging technology with existing materials. Nanotechnology is concept where science, engineering and technology is merged together to get a material with desired properties in nanoscale regime. Nanoscience and nanotechnology has tendency to control individual atoms and molecules by tuning the size of material. Because of the favourable properties such as mechanical strength, higher reactivity, enhanced optical properties nano nanoscale material engineering nano materials are at prime focus. Today, nanomaterials are being extensively explored for their application in energy storage and conversion.²⁻⁵

The rapid increase in global energy consumption and depletion of fossil fuels and hazardous consequences of conventional fuels for our environment, there is need to develop efficient, clean and sustainable energy conversion and storage systems. Over the years, many new techniques have been developed towards clean energy including wind energy, solar energy and hydro energy. Significant amount of work has been done for harnessing the solar energy and wind energy by using solar cells and wind mills, respectively.^{5,7} Since, the time domain of for harvesting renewable sources of energy does not coincides with our practical usage, we need efficient energy storage systems. In response to increase in energy needs it has been realized that energy storage should be much on focus in itself than the energy production. This leads to an increase interest in modifying energy storage systems to increase their efficiencies.^{8,9} Amongst the various avenues available for energy storage the ones that stores electrical energy are the most sought after. Two such electrical energy storage devices which have been for front in regards are rechargeable batteries and Supercapacitors. Supercapacitors work on the similar

principle to that of capacitors but utilize higher electrode surface area and thinner dielectric to achieve higher capacitance values. This allows Supercapacitors to possess higher energy and power density compared to that of traditional capacitors.^{10,11} Mechanism of charge storage in case of super capacitors is the surface adsorption of ions at electrode electrolyte interface and this type of charge storage mechanism is referred to as EDLC. The storage mechanism involves diffusion of ions and have higher powers might be expected from such device. Owing to high power delivery the Supercapacitors can compliment batteries.

1.2 Supercapacitor

In 1957, H. I. Becker designed the first electrochemical supercapacitor (ES). The ES was based on a porous carbon electrode immersed in electrolyte. This was first electrical device using the type of double layer charge storage mechanism arising from non-faradic charge separation at electrode/electrolyte interface. The charge storage mechanism in Supercapacitors matches that of conventional capacitors but the material polarisation in conventional capacitors is replaced by electrolyte polarisation in Supercapacitors. Fig.1 shows the schematic of supercapacitor representing its physical properties. Supercapacitors allow us to manipulate the E.S.R. component thereby enabling us to achieve high power densities. In addition to high power and energy density Supercapacitors also advantages of long cyclability, short charging time and low self discharge rate over electrochemical batteries.¹² EDL behaviour predominantly depends upon on the surface area accessible to the electrolyte ions. The important factors influencing EDL behaviour are specific surface area, pore-size distribution, pore shape and structure, electrical conductivity, and surface functionality. Pore size is critical factor that governs the capacitance and the rate capability. A preferable electrode should have macropores as the ion-buffering reservoir, mesopores (2-50 nm) for promoting ion transport, and micropores (<2 nm) for enhancing charge storage.¹³

In EDLC each electrode can be considered as a single capacitor with capacitance proportional to the surface area A of the electrode/electrolyte interface and to the electrolyte permittivity ϵ .

$$C = \frac{\epsilon A}{d}$$

Total capacitance can be given according to the equation:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$

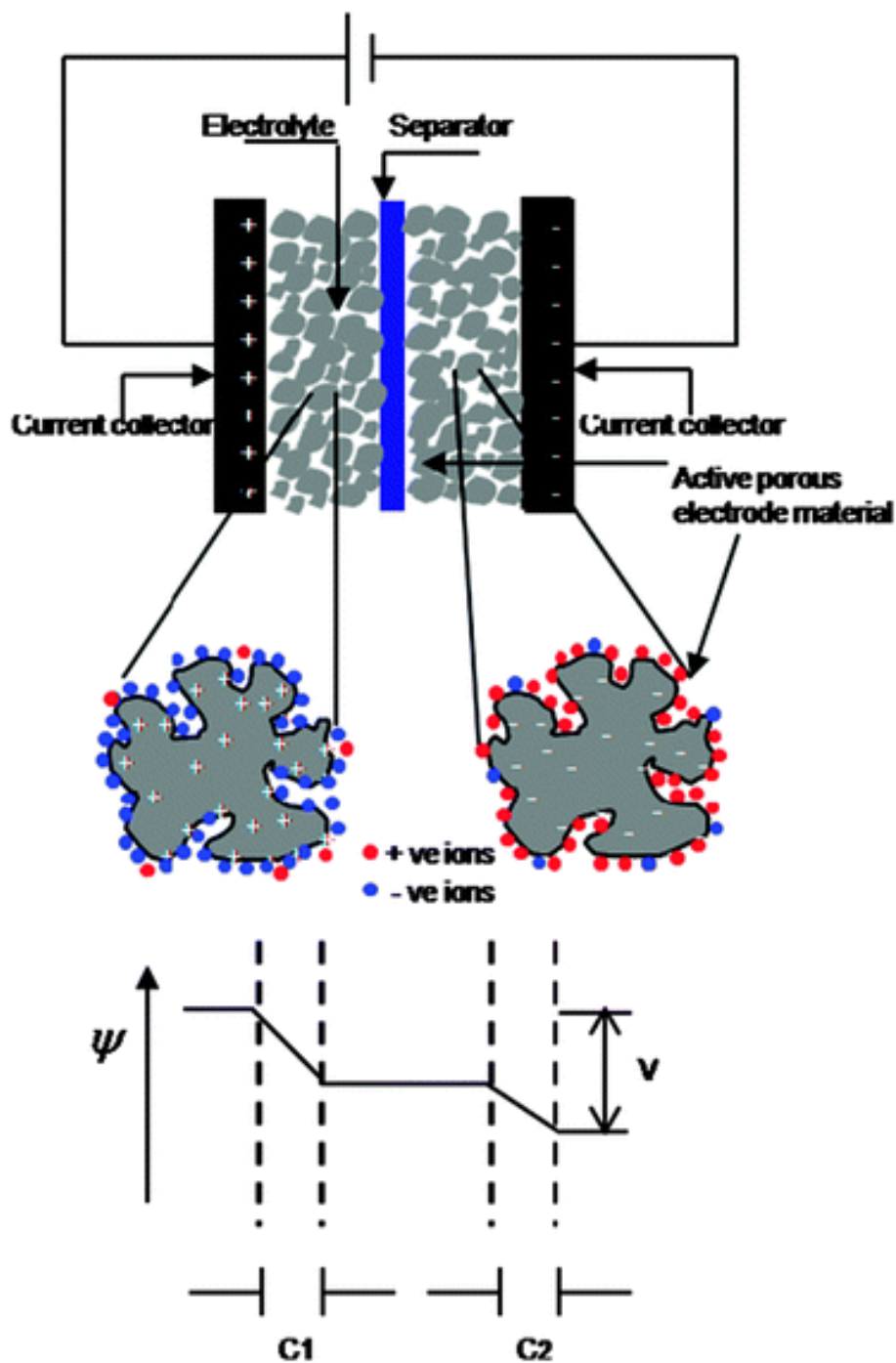


Figure 1: Schematic representation of an EDLC based on porous electrode materials.

(Adapted from Chemical Society Reviews, 2009, 38, 2520-2531)

The energy density and power density are two critical parameters which define the effectiveness of energy storage. The energy density defines the quantity of storage energy while power density defines the rate of energy storage and retrieval.

Energy (E) stored in a capacitor is proportional to the capacitance (C) and voltage (V) across the two electrode of the capacitor. The energy is given as:

$$E = \frac{1}{2} CV^2$$

The power (P) for a capacitor is defined as energy derived per unit from capacitor. The maximum power that can be derived from capacitor is given by the following relation:

$$P = \frac{V^2}{4 \times R_s}$$

Where, R_s is the equivalent series resistance (ESR), it is the combination of resistance from current collector, electrodes and dielectric material.

Figure2 shows the Ragone plot used for performance comparison between various devices in terms of their energy storage and conversion power. The improvement in the performance of the supercapacitor can be assessed with the help of this plot.¹²

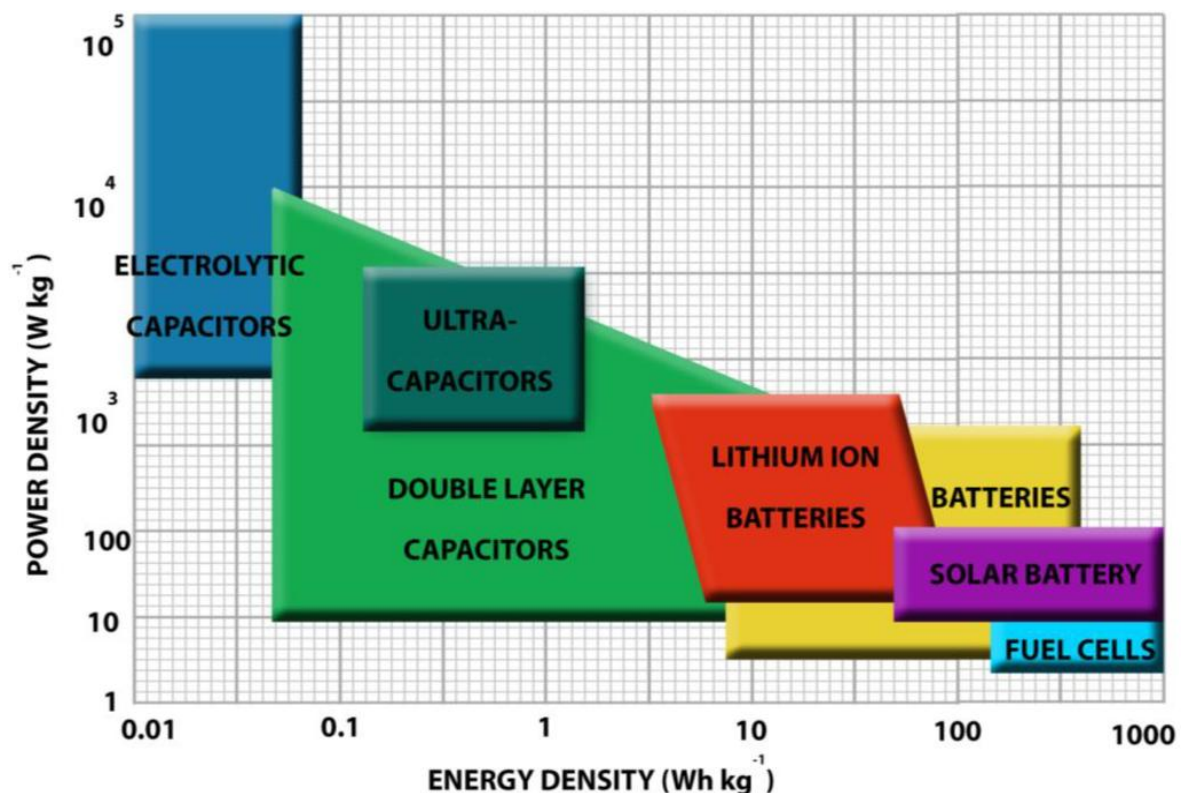


Figure 2: Ragone plot of various energy storage devices

(Adapted from Micromachines 2014, 5(2), 171-203)

From figure2, we can elaborate the challenges for each device, future outlooks and applications in these advanced energy and power system. It can be observed from the plot that Supercapacitors or ultracapacitors occupy a region between conventional and batteries. Supercapacitors have higher energy density when compared to conventional capacitor and higher power density in comparison to batteries. These attributes of Supercapacitors make them more adept to practical applications.

1.3 Classification of Supercapacitors

Supercapacitors can be classified into three major sub classes depending upon the mechanism of charge storage employed in the device.¹⁴ the three major types of Supercapacitors are as follows:

1. Electrical double layer capacitors (EDLCs)
2. Pseudocapacitors
3. Hybrid capacitors

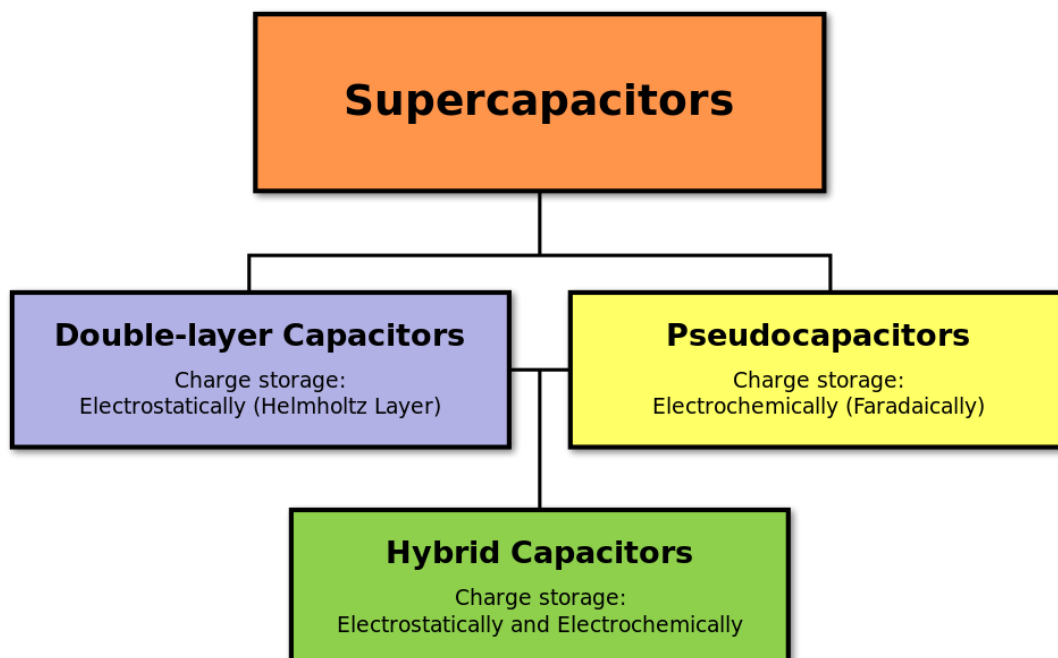


Figure 3: Classification of Supercapacitors

1.3.1 Electrochemical double-layer capacitors (EDLCs): EDLCs are constructed using two high surface area carbon electrodes, an electrolyte and a separator. EDLCs stores electric charge by a non-faradic mechanism in which electric charge gets stored in the Helmholtz double layer which is formed at the interface between the electrolyte and the electrode material, without involving any electron transfer from the electrode surface into the electrolyte or vice versa.^{14,15} when the voltage is applied across the two electrodes of the EDLC, the diffusion of electrolyte ions towards electrodes of opposite polarity takes place. This leads to charge accumulation at the electrode surfaces due to the electrostatic attraction between unlike charges present in the electrolyte and at the electrode. Capacitance value for EDLC is directly proportional to the surface area of the double layer formed; hence activated carbons with high surface area are used to increase the capacitance for EDLC type Supercapacitors. Figure shows the working mechanism for the EDLC type of supercapacitor.

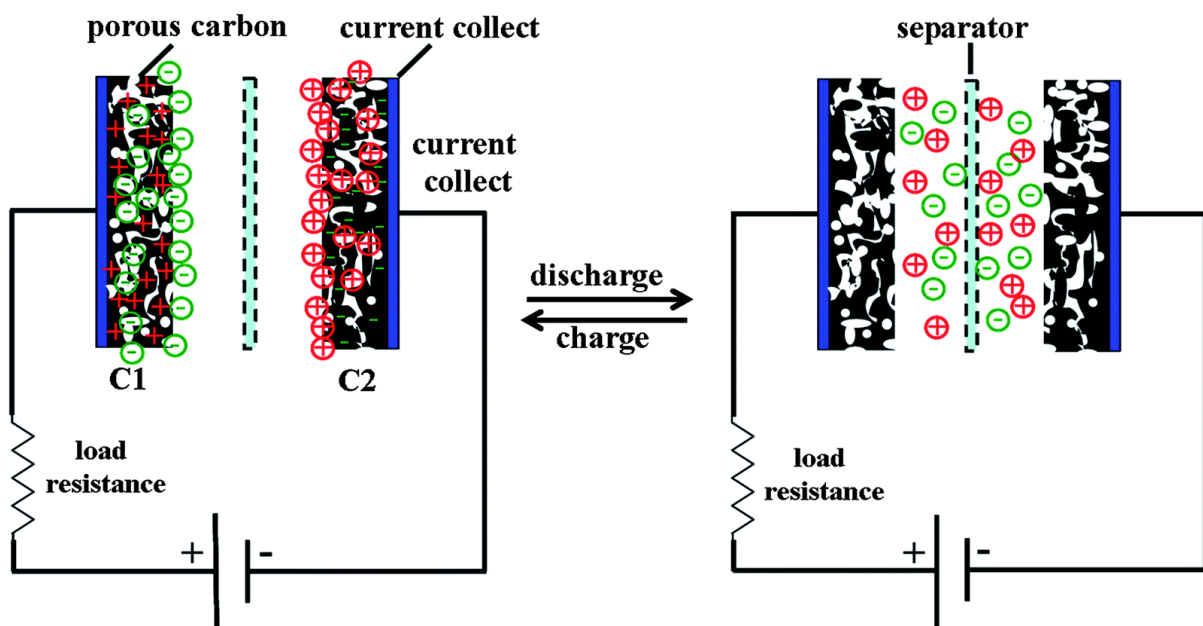


Figure 4: Schematic diagram of charge-discharge of EDLCs

(Adapted from J. Mater. Chem. A, 2014, 2, 4852-4862)

1.3.2 Pseudocapacitors: Pseudocapacitors store electrical energy by faradic mechanism, which is facilitated by electron charge transfer between electrode material and electrolyte by redox reactions, electrosorption and intercalation process. Pseudocapacitors are constructed with electrodes made up of metal oxides or conducting polymers which offer higher faradic pseudocapacitance than the static double layer capacitors.^{8,16}

1.3.3 Hybrid capacitors: A hybrid capacitor is the combination of two different electrodes, one that store charge electrostatically, and the other storing charge faradically.¹¹ Hybrid capacitor exploits the advantage of both EDLCs and Pseudocapacitors in order to achieve higher energy and power density. In such types of Supercapacitors cathode acts as EDLC and anode acts as Pseudocapacitors. Cathode is mostly carbon based materials, while anode is metal oxides, conducting polymers.

1.4 Objective of work

To overcome the challenges faced by the energy storage technology various materials like carbonaceous and metal-oxide materials have been explored for enhancing the performance of the Supercapacitors. For EDLCs, carbon based electrode materials have been intensively investigated. However, EDLCs exhibit relatively low specific capacitance, and this limits their commercial application where higher energy is desired.¹⁴ A large energy density is associated with Pseudocapacitors because of faradic reactions. Hence, there is growing interest in materials having pseudocapacitive nature. Metal oxides/hydroxides, nitrides, sulphides and conducting polymers are investigated as efficient electrode materials in Pseudocapacitors. However, their performance is limited due to low operating voltage window.⁹ Amongst these, transition metal oxides (MnO_2 , Co_3O_4 , RuO_2 , NiO , $\text{Ni}(\text{OH})_2$ etc.) are being widely studied because of their variable oxidation state and ability to store higher amount of energy by ultrafast redox reaction within the potential range of water decomposition.¹⁷⁻¹⁹

Carbon based electrode materials are the most widely used because of the desirable physical and chemical properties. It has various allotropes and due to variety of microstructure, various forms (fibers, composites, aerogels, sheets, hydrogels, monoliths, tubes etc.), a rich variety of dimensionality 0D to 3D offers itself as an

attractive material for supercapacitor application besides the low cost. They are chemically stable in both acidic as well as basic solutions and shows good performance over wide range of temperatures.²⁰⁻²²

Porous Carbon materials prepared by pyrolysis have attracted much attention because of easy synthesis methods and low cost. There are various sources have been used like biomass, waste paper to get highly porous carbon materials.²³ Currently people are using various doped carbon, like Phosphorous, nitrogen etc. to enhance the pseudocapacitive behaviour of the Supercapacitors. The applicability of nitrogen doped porous carbon material has increased in supercapacitor application.²⁴ Various materials have been reported with nitrogen precursors like urea and melamine to get nitrogen doped porous carbon by controlled pyrolysis and also PVA, PAN, poly acryl amide and polyaniline polymer precursors containing nitrogen have been studied.²⁵⁻²⁹

Carbonaceous materials (activated carbons, template carbon, and carbon aerogels) having porous structure and high surface area have been widely studied as supercapacitor electrode material. Among these, carbonaceous hydrogels have been widely investigated for application as electrode materials for Supercapacitors and batteries, adsorbents and sensors because of their flexibility, excellent osmotic property, light weight and high water absorptivity. Carbonaceous gels have an open porous structure and 3D network which helps in stable and sustainable transport of electrolyte ion and electrons to the surfaces which are very promising in supercapacitor applications.^{30,31}

Over the past few decades, many carbonaceous hydrogels and aerogels (graphene based hydrogels and aerogels, polymer derived aerogels, biomass derived hydrogels and aerogels and carbon nanotube based aerogels) have been synthesized for supercapacitor applications. Recently, biomass derived carbonaceous hydrogels are of great interest for supercapacitor with characteristics flexibility, large capacitance and light-weight. Metal oxides and Conducting polymers are introduced into the network of the gels to improve the capacitive nature of the carbonaceous gels.³¹⁻³³

Quality of carbon (surface and textural properties) depends upon type of carbon precursor and method employed for the preparation. Porosity of carbon material can be controlled by activation (physical and chemical) and template based method to some extent. The choice of pyrolysis parameter such as temperature, time and activating agent determine the micro porosity of the carbon, by tuning these we can control the size of pores. Template based method is most reliable as it control the size of pores and also gives connectivity between them which helps in smooth transfer of charges and ions.

In this report, presented work is to study carbon materials synthesized from natural and synthetic precursor in Supercapacitors application. Our work on yogurt as a precursor for the supercapacitor has been published in Journal of material chemistry A paper “Yogurt: a novel precursor for heavily nitrogen doped supercapacitor carbon” in which I am co-author for my contribution towards the project. We used various natural gels (pectin, alginate and Alovera) as a precursor to get carbon for the supercapacitor application.⁴¹ Here my focus is on pectin derived carbon which gives best performance among other natural gel carbons which are comparable to reported literature.

2. Characterization techniques

2.1 X-ray Diffraction

X-ray diffraction (XRD) is a technique used for the understanding of structural information of materials. XRD can provide information regarding crystal structure, phase purity, lattice parameters, crystallite size and defect in the lattice of materials. For the XRD measurements, monochromatic beam of x-ray made to be incident on the target material at various angles (θ). When the x-ray strikes the target material it get scattered and undergo constructive or destructive diffraction pattern depending on the angle by which it get diffracted. Constructive diffraction pattern occurs on certain angle for particular plane, which satisfy the Bragg's law. Bragg's law is given by

$$2d\sin\theta = n\lambda$$

Bragg's condition is satisfied when path difference is the integral multiple of the wavelength of x-ray used.^{35, 36} Figure 5 shows the schematic representation of the X-ray diffraction technique.

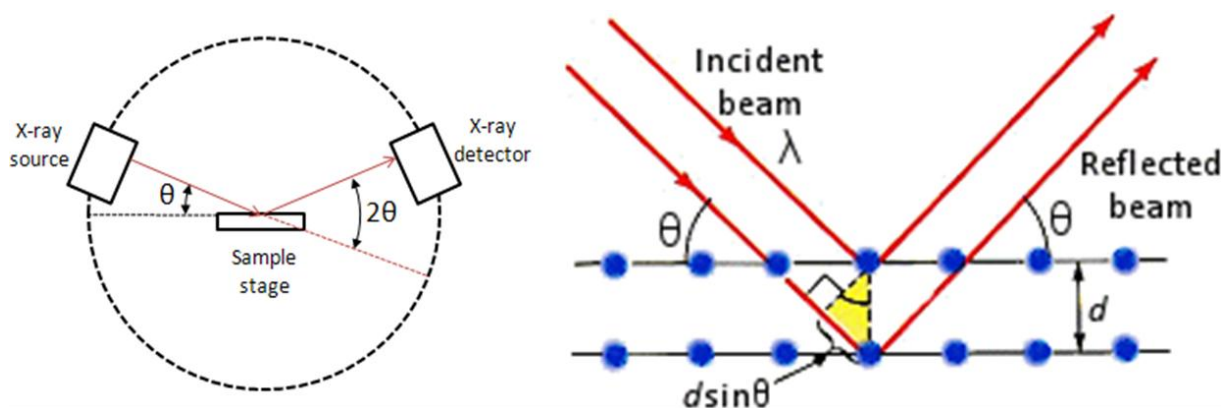


Figure 5: Schematic of X-ray Diffraction technique

The samples were characterized to see the defective nature of carbon with the help of XRD. The XRD measurements were carried out at room temperature using a Philips X'Pert PRO diffractometer with nickel-filtered Cu K α radiation at National Chemical Laboratory (NCL), Pune.

2.2 Raman spectroscopy

Raman spectroscopy is a technique which can provide chemical and structural information of materials. It is used to observe low frequency modes in a system.³⁷ It is helpful in quality control in carbon materials. Raman spectroscopy can provide information regarding defect, doping, purity and strain in materials. In Raman spectroscopy sample is illuminated with a laser beam in the ultraviolet (UV), visible or near infrared range. The laser light excites the molecular vibrations, phonons in the system, this changes the energy of the photon leads in the shift. The shift in energy gives information about the different vibration modes. The scattered light is collected by lens and sent through the spectrophotometer to obtain Raman spectrum. The Raman spectroscopy was performed using a LabRAM HR800 from JY Horiba with laser excitation wavelength of 532 nm.

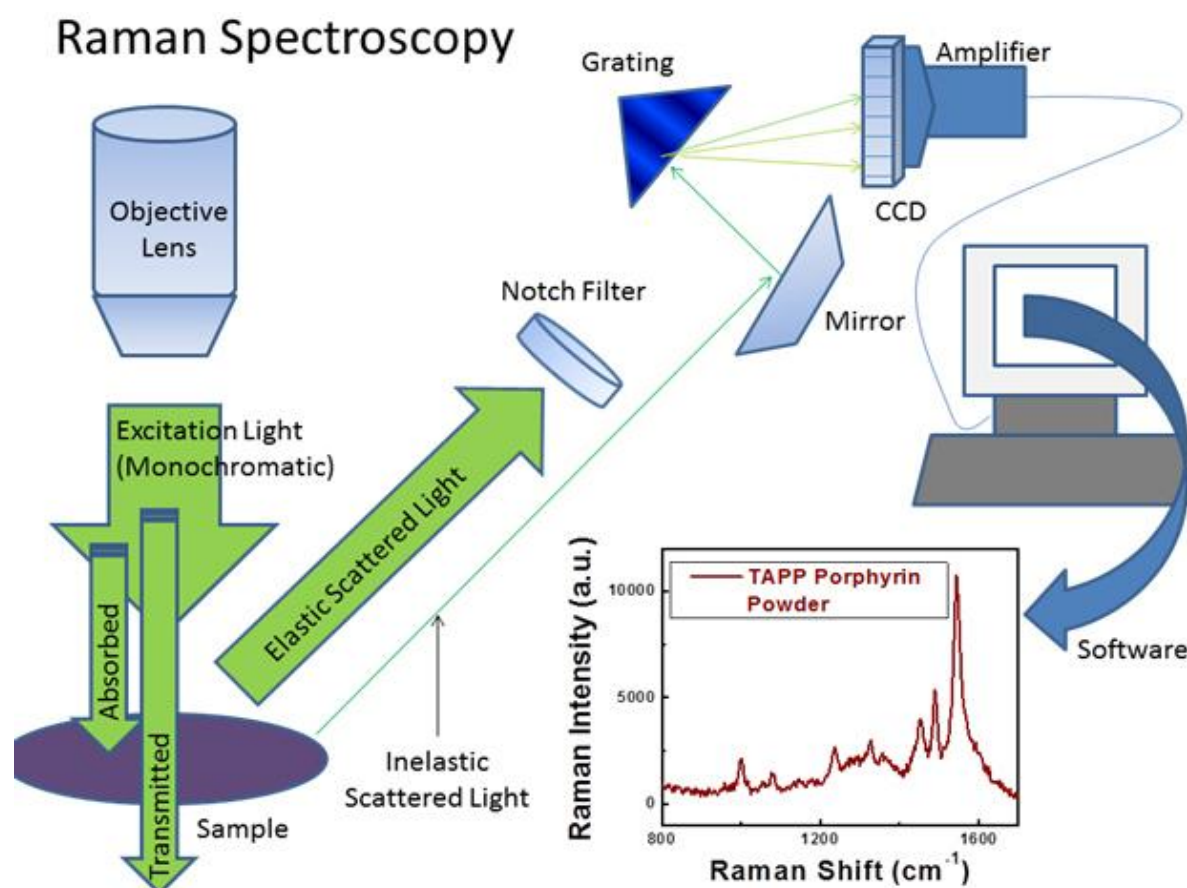


Figure 6: Schematic diagram of Raman spectroscopy

(Adapted from http://www3.nd.edu/~kamatlab/facilities_spectroscopy.html)

2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) based on scattered electrons from sample. It reveals information about the surface morphology and composition of materials. It can be used to analyze the surface roughness, porosity, grain size, particle size distribution and material homogeneity. In SEM, electron beam is produced either by thermal emission source or field emission cathode. Scanning electron microscopy forms image by collection of back scattered electrons which revert from a focussed electron beam scanned over the sample. This image is displayed on the screen which is located inside the instrument. Figure 7 shows the schematic representation of the SEM instrument. The morphology of the prepared samples was analyzed using Nova Nano SEM 450 at NCL, Pune.

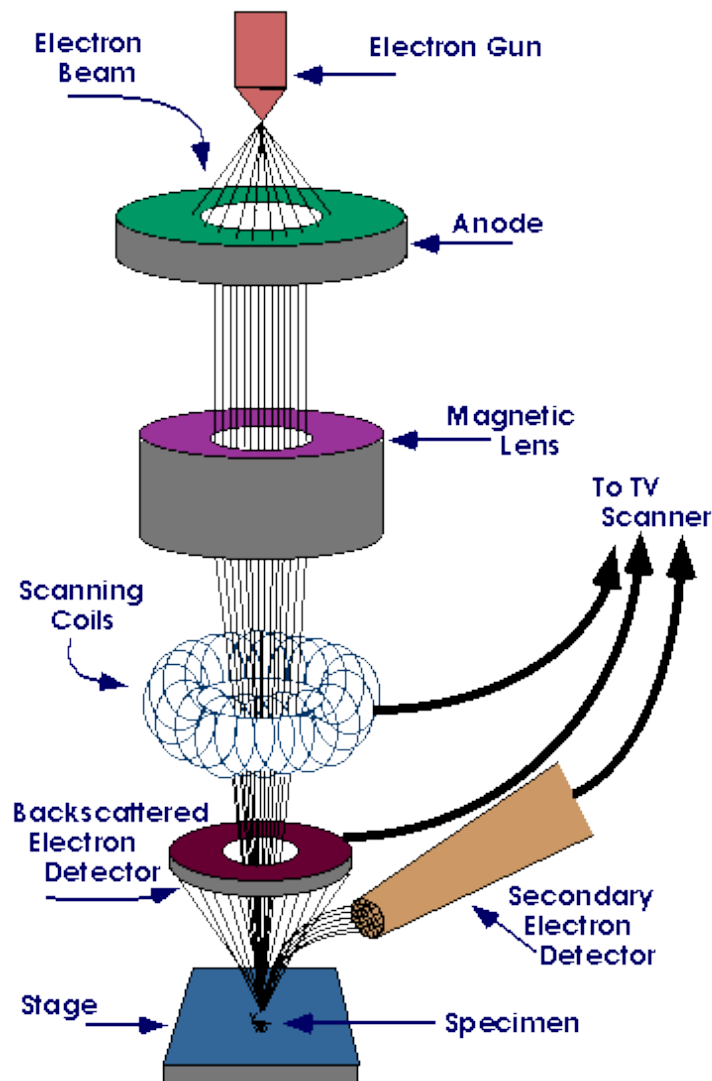


Figure 7: schematic representation of SEM

(Adapted from <https://www.purdue.edu/epps/rem/rs/sem.htm>)

2.4 Transmission electron microscope

Transmission electron microscope (TEM) uses high energy electron beams to provide morphological, compositional, crystallization and even magnetic domains information of the specimen. TEM is used for imaging of dislocations, grain boundaries and other defect structure in the solids. In TEM, high energy electron beam is focussed on the sample, these electrons interact with sample and some are transmitted through it. The transmitted electrons are collected by detector to form an image on the fluorescent screen. Figure shows the schematic representation of TEM. Particle size and morphological details were investigated by the TEM. TEM was performed on a IFEI Technai 30 system microscope operated at 300 kV and 119 μ A.

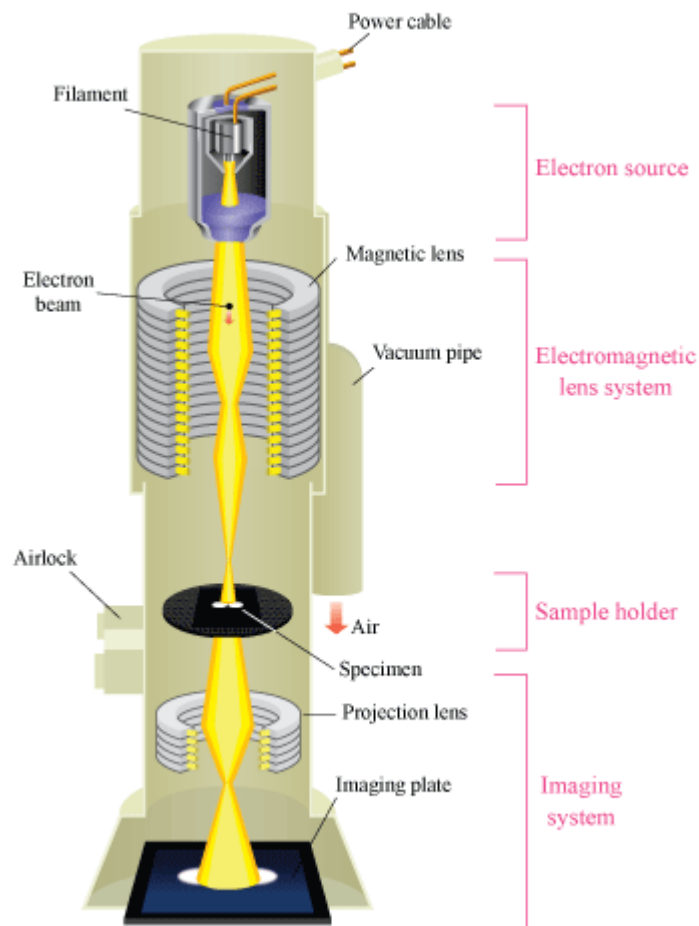


Figure 8: Schematic representation of TEM.

(Adapted from http://www.hk-phy.org/atomic_world/tem/tem02_e.html)

2.5 Brunauer- Emmett- Teller surface area analysis

Brunauer-Emmett-Teller (BET) theory explains the physical adsorption of gas molecules on the solid surface. It is also used to determine the surface area and pore size distribution of porous materials. BET analysis gives specific surface area of materials by measuring nitrogen multilayer adsorption as a function of relative pressure. This technique sums up the external area and total area of all the pores to determine the total specific surface area. This is helpful in to get the information for studying the effects of surface porosity and particle size in many applications.

The BET measurements were performed using N₂ adsorption – desorption isotherm in a Quadrasorb automatic volumetric instrument (Nova 3200 e) surface area and pore size analyzer.

2.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to investigate the chemical composition on surfaces. The XPS measure the kinetic energy of all the collected electrons. In XPS, a monochromatic x-ray beam emits the photoelectron from the surface of sample. These photoelectrons are dispersed according to their kinetic energy by electron energy analyser and analyzed in vacuum to avoid gas phase interference. The XPS contains only the information about the top 10-100 Å⁰ of the sample. The binding energy can be determined by the peak positions and hence element present in the sample.

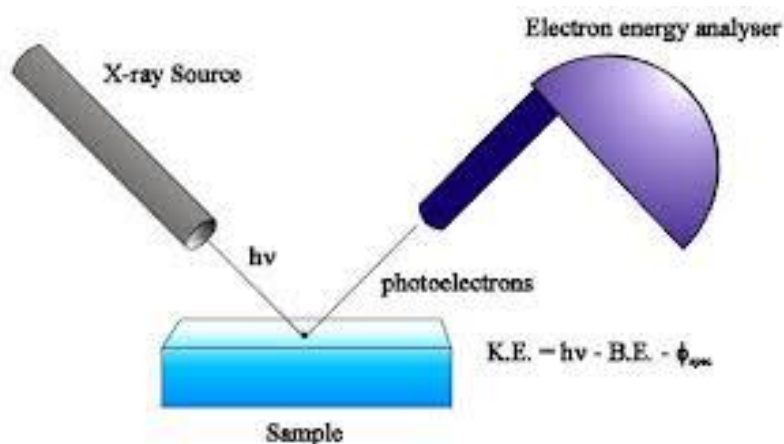


Figure 9: Schematic of X-ray Photoelectron Spectroscopy

(Adapted from <https://wiki.utep.edu/display/~anarayanawamy/X-ray+Photoelectron+Spectroscopy>)

For our work, XPS was performed by VG scientific ESCA-3000 spectrometer using non-monochromatized Mg K α radiation (1253.6 eV) at a pressure of about 1×10^{-9} torr.

2.6 Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical technique to measure the current as a function of potential that develops in an electrochemical cell. In CV, voltage of working electrode is swept between two values at fixed rates. However, at specific potential (V_2) scan is reversed and the voltage is swept back to initial potential (V_1). Figure 10 shows typical cyclic voltammograms recorded for reversible single electrode transfer reaction. CV thus involves a plot of voltage developed at working electrode (measured against a reference electrode) and current generated (measured between working and counter electrode) in the circuit. From figure it can be seen that the peak on the current axis is generated for the analytes that are proven to reduction in the range of potential being selected for the forward scan.

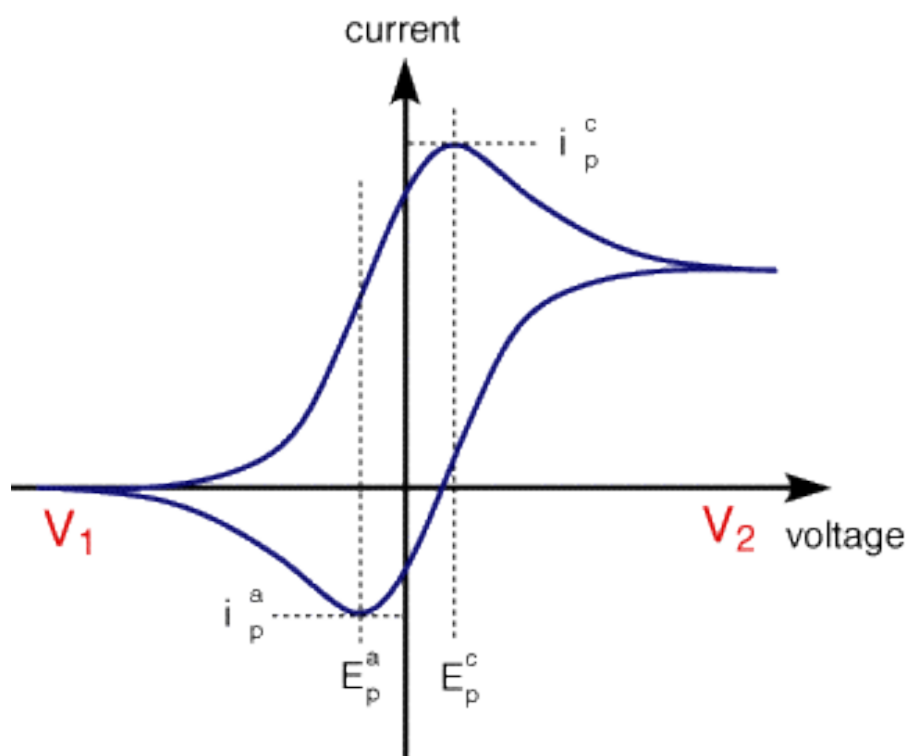


Figure 10: A typical cyclic voltammograms

(Adapted from <http://www.ceb.cam.ac.uk/pages/linearsweep-and-cyclic-voltametry-the-principles.html>)

The corresponding current will show a maximum as the potential reaches to reduction potential of analytes, the value of peak current at this potential is referred to as cathodic current. The current value starts falling after this owing to depletion of analytes concentration near the electrode surface. After switching potential, it will reach at potential where it re-oxidize and produce the current of opposite polarity that of the product formed in the reduction process. The oxidation peak usually has similar shape as that of reduction peak. Cyclic Voltammetry provides a wide range of information about the electrode and electrode/electrolyte interaction and the nature of the cyclic voltammograms depends upon the types of measurements for desired applications.

2.7 Galvanostatic charge discharge for capacitance and stability measurement.

Galvanostatic charge-discharge measurement is a Chronopotentiometry technique which is used to characterize the electrochemical properties of insertion materials.

This technique measures the voltage response of a working electrode material to the constant current (charging or discharging) pulse. The plot generated will be thus a voltage vs. time measured at constant current pulses. The technique is used for testing the performance of a material for supercapacitive applications. The materials which withstand high charging and discharging current loads for longer time are correlated with high capacitive performances. The curve provides charge discharge time for capacitor from which the capacitance and stability can be calculated. The capacitance is calculated using following equation:

$$C_s = \frac{I \times \Delta t}{m \times \Delta V}$$

Where, C_s is specific capacitance (F/g), I is the current (A), Δt is discharge time (s), m is the active mass of material, and ΔV is potential drop during discharge (V).

The cyclic voltammetry and other electrochemical characterizations were performed by AutoLab PGSTAT 30, eco-chemie.

3. Chemical activation of carbon precursors for synthesis of porous carbon materials for supercapacitor application.

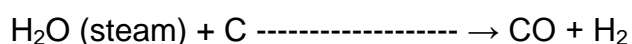
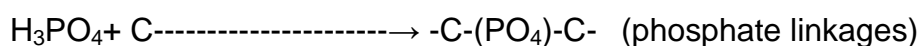
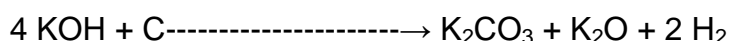
Pyrolysis is a high temperature thermolysis (*thermo*= heat, *lyses* = breakdown) process of organic matter which leaves solid carbon as residue. This process also referred as **carbonization**. This process is clearly distinct than other high temperature reactions of organic matter like combustion and hydrolysis in being exclusively an oxygen free process and thus only minimal amount of carbon is lost from the back bone, unlike combustion where oxygen drives all the carbon in to gaseous carbon dioxide. High temperature excited state pyrolysis reactions of organic matter removes most of the functional groups and heteroatom from the backbone and shapes the left over carbon materials in to ordered semi-graphitic regions. Graphitization thus achieved gives conductivity to carbon material and makes them suitable for electrochemical applications.³⁸

3.1 Pyrolysis and Activation for synthesis of porous carbons.

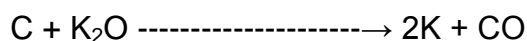
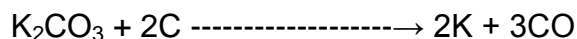
As mentioned in chapter 2 capacitance of material is related to the surface area of the material through the equation, $C = \epsilon A/d$, for a sufficiently conducting material. In this regard the porous carbon materials are holding a centre stage as super-capacitive materials being sufficiently conducting and having actual surface area 500-1000 times higher than apparent surface area. Pyrolysis reaction is easiest and cheapest route for the synthesis of high surface area carbon. High temperature $>700^{\circ}\text{C}$ inert atmosphere reactions are suitable for synthesis of semi graphitic conducting carbon materials. The materials synthesised by such simple process alone in absence of addendum are usually not high surface area and yield low surface area hard carbon materials. These hard carbon materials although conducting don't usually have high surface area to be of any use for super capacitor but may be useful for some other energy storage purposes like Na^+ ion battery. Thus we need to add some external agent which can perturb the temperature induced carbon ordering process by participation in some carbon etching reactions at high temperature. The simultaneous effect of parallel running temperature induced ordering and external agent induced disordering process leads towards the synthesis of porous conducting carbon materials with high enough surface area to be extremely useful for the supercapacitor application. The pyrolysis reaction thus carried out is called **Activation Reactions** and the external agents which carries out

the activation is called activating agent. Most commonly used activating agents are KOH, NaOH, ZnCl₂, H₃PO₄ and steam, NH₃, and CO₂ etc.³⁹⁻⁴⁵

3.2 Chemistry of activation: Chemically activation process is high temperature reaction of carbon atom with the activating agent to form gaseous products of carbon or carbonate salts of metal which can leave the reaction site or can be washed away later on. The departure of carbon from the site leaves the pore which can deepen or broaden depending upon the reaction conditions. The chemical reactions of some common activation agents are listed below:



It must be noted that by products of reaction in case of KOH can further participate in carbon etching by following reactions and thus can lead to deeper and much wider pores than other activating agents.



3.3 Activation of some novel natural and synthetic precursors towards synthesis of porous carbons for supercapacitor applications

Novel supercapacitor grade carbon was synthesized from a natural precursor, natural gel (Pectin), by a simple activation reaction. The optimised results for gel and KOH 1:1 weight ratio results are shown here. The carbon material thus synthesised showed the typical nature of a turbostratic nature carbon, with presence of high density of micropores and material delivered a capacitance of 310F/g at 1A/g in aqueous medium.

4.3.1 Materials used

All the chemicals used for the synthesis were analytical grade and commercially available and were used as received without further purification.

3.3.1 Synthesis of carbon material: The gel powder and KOH in 1:1 weight ratio was mixed together in the mortar and pestle. The paste so obtained was dried in a vacuum oven at 100⁰C for 6 hrs. The resulting dry mixture was subjected to pyrolysis reaction in a tube furnace under the constant argon flow. The pyrolysis conditions were set at scan rate of 3⁰C/min, temperature of 800⁰C, and duration of pyrolysis for 3hrs. The pyrolysis product was washed with Concentrated HCl with 6hrs stirring followed by removing the extra acid and water soluble impurities by filtration in a vacuum driven filtration assembly. Solid carbon material was collected and dried in vacuum oven at 900⁰ for 24 hrs. The final carbon was characterised further before subjecting it finally to electrochemical measurements.

3.3.2 Preparation of electrode materials

The electrode was prepared by coating a slurry of 80 wt% carbon material (sample), 15 wt% carbon black and 5 wt% polyvinylidene difluoride (PVDF) in N-methylpyrrolidone on 1 cm² area of carbon fibre paper strip (1×3.5 cm²) and then drying at 90⁰C for 24 hrs.

3.3.3 Results and discussions

Figure 11 shows the FE-SEM images of carbon material synthesised at different resolutions. As can be seen from figure 11 a) & b) that the material comprises of micron dimensional sheets of carbon connected together to give a particular 3-D morphology. High resolution images figure 11 c) & d) show that carbon micro sheets have uniform microporosity seen as small white dots on the sheets. Small white coloured patches reveal that some unwashed impurities are lying non-uniformly distributed over the carbon sheets. For further characterization of the carbon sheets X-Ray Diffraction (XRD) measurements were done and diffraction pattern was recorded. Figure 12 shows the XRD pattern of the carbon material. The material shows two broad peaks at 23.4⁰ and 43.3⁰ indexed to 002 and 101 planes of graphite. The peaks are broad enough depicting turbostratic nature of the carbon, which is common for pyrolysis temperature chosen. Peak position of 23.4 means the interplanar separation of 0.37 nm (as per Bragg's formulae) compared to 0.34nm for graphite. Thus the small graphitic domains created at this pyrolysis temperature are having vertical disorder in addition to the longitudinal disorder.

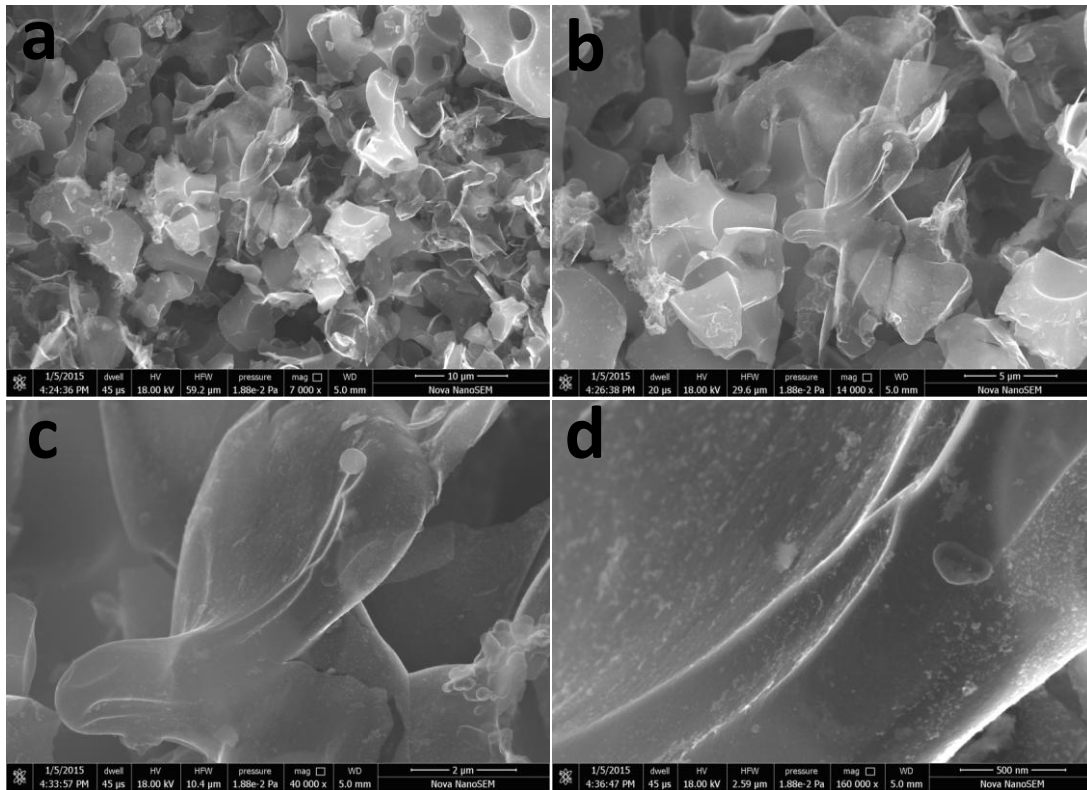


Figure 11: a) & b) shows FE-SEM images of pectin derived carbon. c) & d) shows the TEM images of pectin derived carbon.

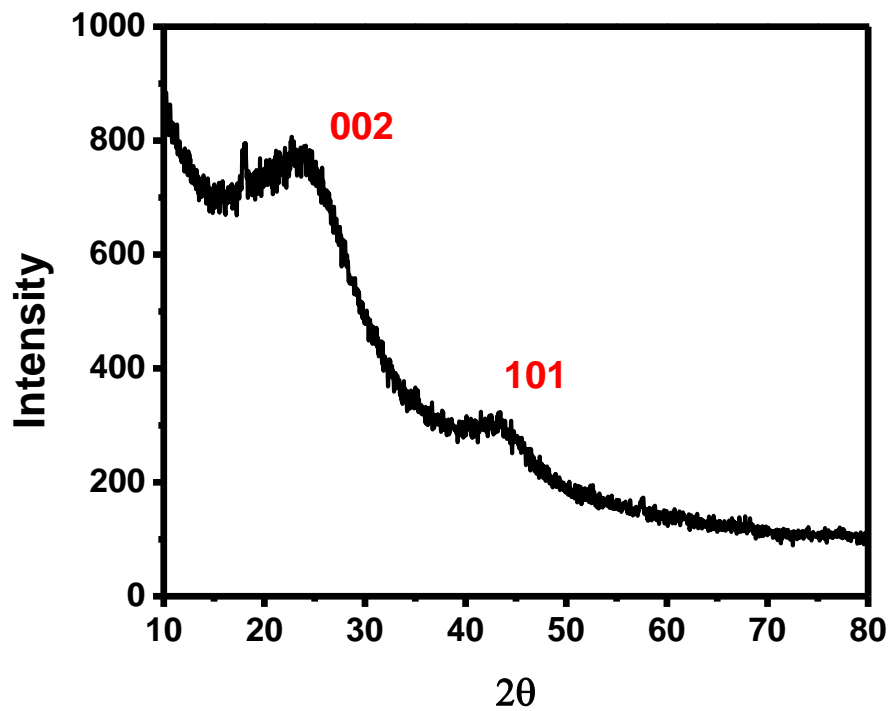


Figure 12: XRD Plot of pectin derived carbon

Electrochemical performance of the carbon material mounted on carbon fibre was checked in 1M H₂SO₄ solution in a 3- electrode system using platinum strip as a counter electrode and Hg/Hg₂Cl₂ as reference electrode.

Figure 13 shows the electrochemical performance of carbon material. Cyclic voltammetry, charge discharge, and impedance plots were thoroughly analysed for capacitance calculations. Fig 13a shows the cyclic voltammetry plots of our carbon material at different scan rates ranging from 200mV/s to 10mV/s. Nearly vertical side lines of the CV plots show the ideal EDLC capacitor behaviour. The upper and lower borders of the CV loop are wavy this depicts the faradic contribution to capacitance.

Charge-discharge curves in figure 13b show the nearly triangular loops depicting Ideal EDLC behaviour. Further capacitance calculated from charge-discharge are as 310F/g at current density of 1A/g, 260F/g at 2A/g, 250F/g at 5A/g, 230F/g at 10A/g, and 210A/g at high current density of 20A/g. These results are superior than reported for most of the carbon materials synthesised by activation. Figure 13c shows the Nyquist plot of the presented carbon material as can be seen that material has fairly low ESR of 1.56Ω which is considered good for such applications.^{46, 47} Further the semicircle depicts some amount of charge transfer reaction contribution to capacitance and vertical line in low frequency region (which is toward right side) again proves ideal EDLC behaviour.

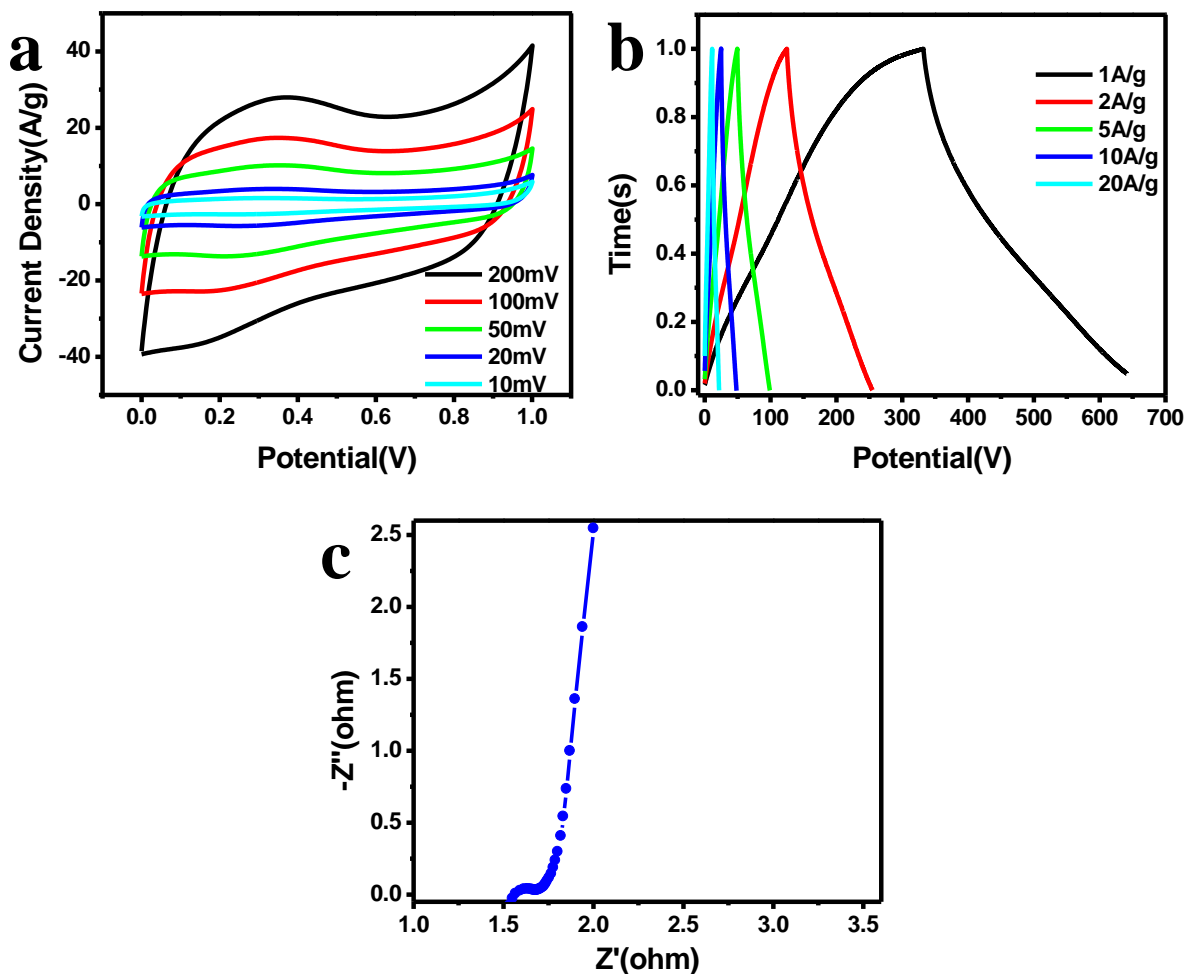


Figure 13: Electrochemical performance of pectin derived carbon. a) CV plots at different scan rates, b) charge-discharge at different current density, c) Nyquist plot

3.3.4 Conclusion

In summary, a new cheap and easily available natural precursor was subjected to KOH based activation reaction and high capacitance of 300F/g was obtained which is comparable and in most cases better than reported values based on activation reaction for supercapacitor application.

4. Porous carbon synthesis based on template method.

4.1 Physical methods for generating pores in carbon materials

Pyrolysis can also be combined with physical methods to generate the porosity in the carbon materials. And there are plenty of them mentioned in the literature.⁴⁸ The most common among them is the addition of inert nano dimensional particles during pyrolysis and subsequent removal of these particles by suitable chemical agents leaving the holes/pores of equal size in the carbon materials. The physical agents used should have the property of easy removal by simple chemical methods. The most commonly used particles are silica particles (ludox, metal particles, metal salt nano particles etc). Sang Hoon Joo et al. infiltrated furfuryl alcohol inside SBA-15 and successfully carried out the polymerization inside the pores. Infiltration of readymade resorcinol gel inside the mesoporous channels and the energy storage application of the corresponding carbon material has been reported very recently.^{49,}⁵⁰ Second and equally common is the template based pyrolysis which involves infiltration of a material into a porous template followed by pyrolysis there in. Final carbon material is liberated by dissolution of particular template. The carbon material thus obtained has reverse porosity of parent mould used. The commonly used moulds are CaCO_3 , organic soft templates, Silica templates (SBA, KIT, MCM) etc.⁵¹ WE have done two problems one with each of the above mentioned methods to synthesise high surface area from some novel precursors, in both experiment we got an efficient super capacitor grade carbon as is discussed in section 4.3.

4.2 Advantages and disadvantages of the physical methods over activation

The physical methods of pore generation in the carbon materials have both superiority and limitation over the chemical activation methods as far as their use in supercapacitor performance is concerned. The differences in the final capacitive performance are related to differences in the structure, dimension, frequency and architecture of pores generated. The main differences in the pores generated by two methods will be in pore diameter. Pores generated by physical methods will be mesoporous having diameter $>2\text{nm}$ as the inert nano particles being used can rarely be below 2nm range and templates having the porosity below 2nm are rare too. On the other hand with chemical methods we can go to porosities of 0.5nm and

below, but mesoporosity is rarely achieved if it is not very heavy activation or a very strong activating agent like KOH which goes for double or triple activation in one go. For super capacitors although microporosity is sought for higher capacitance values because of matching of pore dimensions with that of ions but for higher power delivery the mesopores hold the key because of easy ion insertion and extraction through the pore. Although we get a large density of micropores with chemical activation but there is a good amount of carbon material that lost by release of CO and CO₂ driven by activation reactions. That means that physical methods possess the advantage of material saving during pyrolysis. Further the porosity generated by physical methods adds hierarchical mesoporosity which is good for high power delivery from a supercapacitor but the porosity generated by chemical methods is uniform as far as size of pores is concerned. Thus from the above discussion we can conclude that combination of the physical and chemical methods together can be a best strategy to maximize the performance of material.^{52, 53}

4.3. Synthesis of hierarchical porous carbon material by pyrolysis of a natural polymer in presence of silica nano particles.

4.3.1 Materials used

All the chemicals used for the synthesis were analytical grade and commercially available and were used as received without further purification.

4.3.2 Synthesis of carbon material

2.5ml of 40 wt % Ludox solution containing silica particles of 10-30nm was dispersed in 30ml of water and was stirred for 2-3 hrs to get a uniform dispersion. Then 3g of natural gel powder extracted from apple was added to the dispersion and was stirred for 12hrs so as to get the particles uniformly distributed in the gel matrix. The silica loaded gel was then kept for gentle drying at 60⁰C in vacuum oven. The dried gel was collected and kept for pyrolysis at 800⁰C for 3hrs; temperature of 800⁰C was reached through the temperature scan of 5⁰C. The resulting powder was washed with HF (40%) which dissolves the silica particles leaving the porous carbon material with mesoporous of 10nm to 20nm. The material was subjected to further characterisation and finally to electrochemical performance.

4.3.3 Preparation of electrode material

The electrode was prepared by coating a slurry of 80 wt% carbon material, 15 wt% carbon black and 5 wt% polyvinylidene difluoride (PVDF) in N-methylpyrrolidone on 1 cm² area of carbon fibre paper strip (1×3.5 cm²) and then drying at 90 ⁰C for 24 hrs.

4.3.3 Results and discussion

Figure 14a & b) shows FE-SEM images of the carbon material synthesized here at different resolutions. It is worth noting that carbon material is in the form of carbon net with exclusively the mesoporosity and mesoporosity is in the range of 10-20nm as shown by the high resolution images shown in figure 14c & 14d) the porosity can be referred to as the hierarchical porous structure.

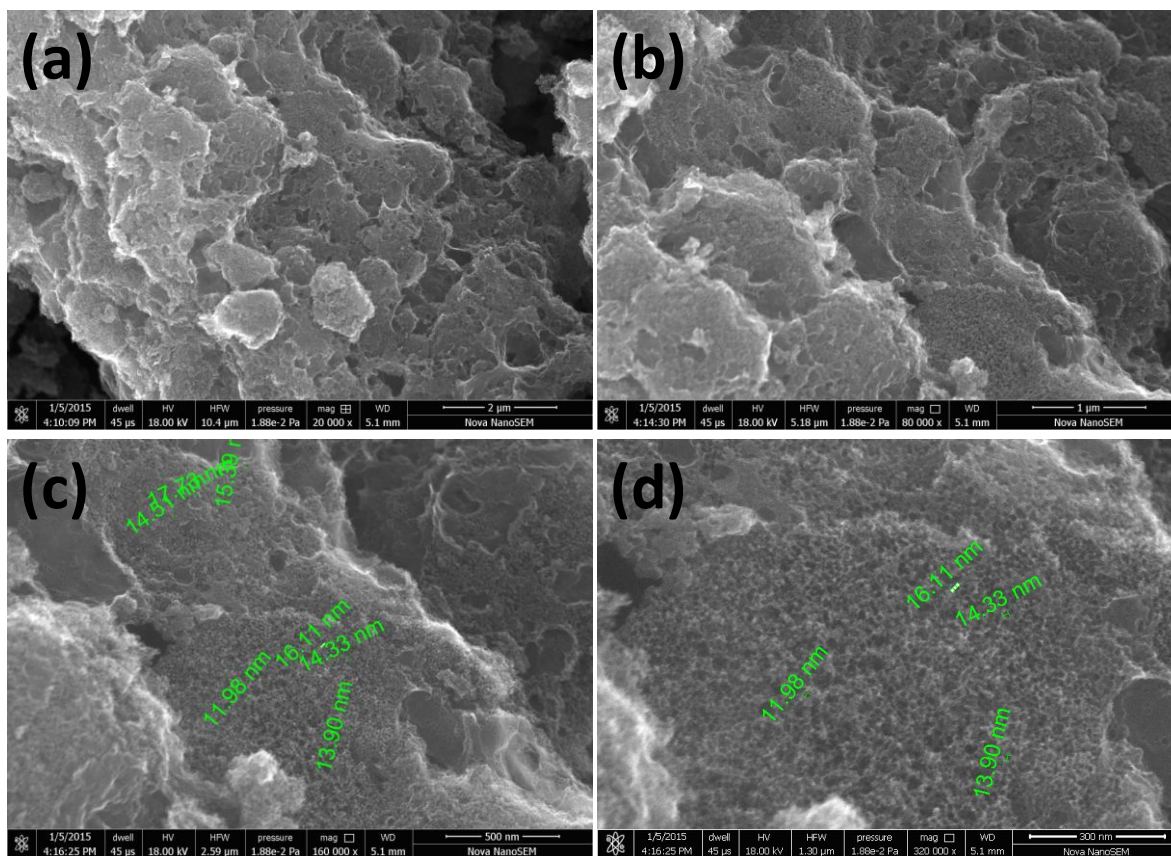


Figure 12: a) & b) shows the FE-SEM images of sample, c) & d) shows the TEM images template based carbon.

Porous architecture was further confirmed by BET surface area analysis and subsequent pore size distribution. Figure 15 shows the BET isotherm of carbon material. BET surface area of the carbon material is $834\text{m}^2/\text{g}$ was calculated. The isotherm is typical IUPAC Type IV with Hysteresis at $P/P_0 = 0.8-1.0$ which is characteristics of mesoporosity with closed pores. Further the pore size distribution plot shown in the inset of Figure 4.2 shows the mesoporosity distributed at around 10nm and having a distribution up to 20nm besides having a small but sharp microporosity centred at 1.2nm. Further to characterise the material at molecular dimensions XRD and Raman analysis was performed. Figure 16 a) and b) shows the XRD and Raman spectra performed for the carbon material, respectively. XRD pattern shows the presence of peak at 25.7° and 43.7° assigned to 002 and 101 graphitic planes. The position of 002 peak points to the inter planner separation close to 0.34nm which is characteristics of graphite. Thus there is nearly perfect order in semi graphitic domains of carbon. Raman spectra shows the two typical

peaks of carbon materials centred at 1320cm^{-1} and 1600cm^{-1} assigned to D-Band and G-Band of graphite.

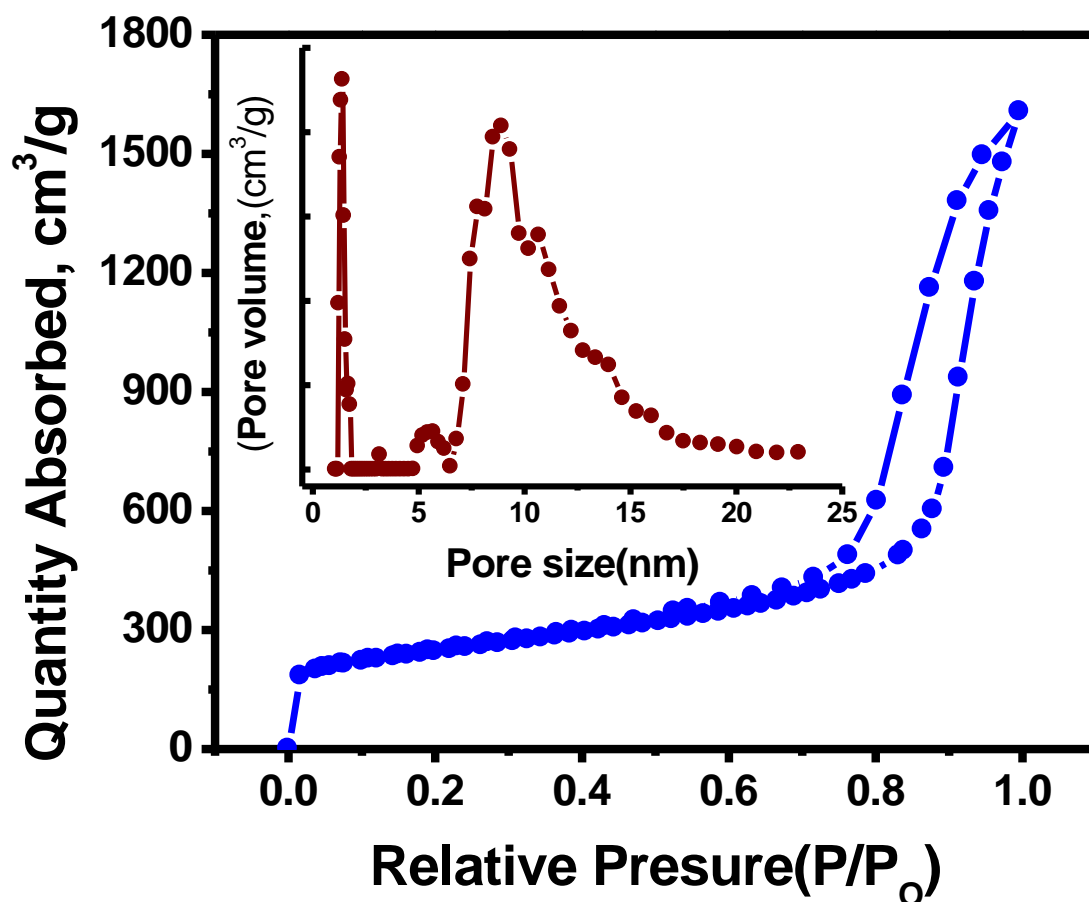


Figure 15: surface area and pore analysis using N_2 adsorption-desorption analysis of carbon using template method

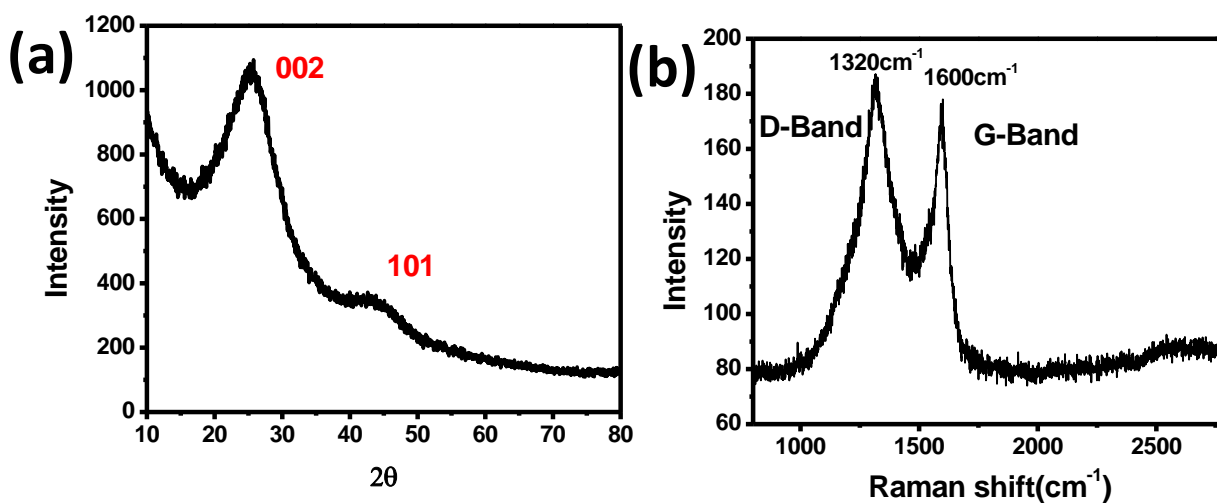


Figure 16: a) XRD plot of pectin derived carbon, b) Raman spectra of pectin derived carbon using template method.

Further I_G/I_D ratio of 0.85 means a graphitization close to graphite as can be concluded from peak heights and complements the XRD data. High surface area with sufficient graphitization hints the better super capacitive performance carbon material.

Figure 17 shows the electrochemical performance was tested in the 3-electrode assembly in $1\text{M}\text{H}_2\text{SO}_4$ with platinum strip as a counter electrode and $\text{Hg}/\text{Hg}_2\text{Cl}_2$ as a reference electrode. Figure 17a shows the cyclic voltammetry loops of carbon material in the voltage scan rate of $200\text{mV}/\text{s}$ to $5\text{mV}/\text{s}$. The rectangular shape of the CV loops shows ideal capacitor behaviour with little contribution from faradic reactions.

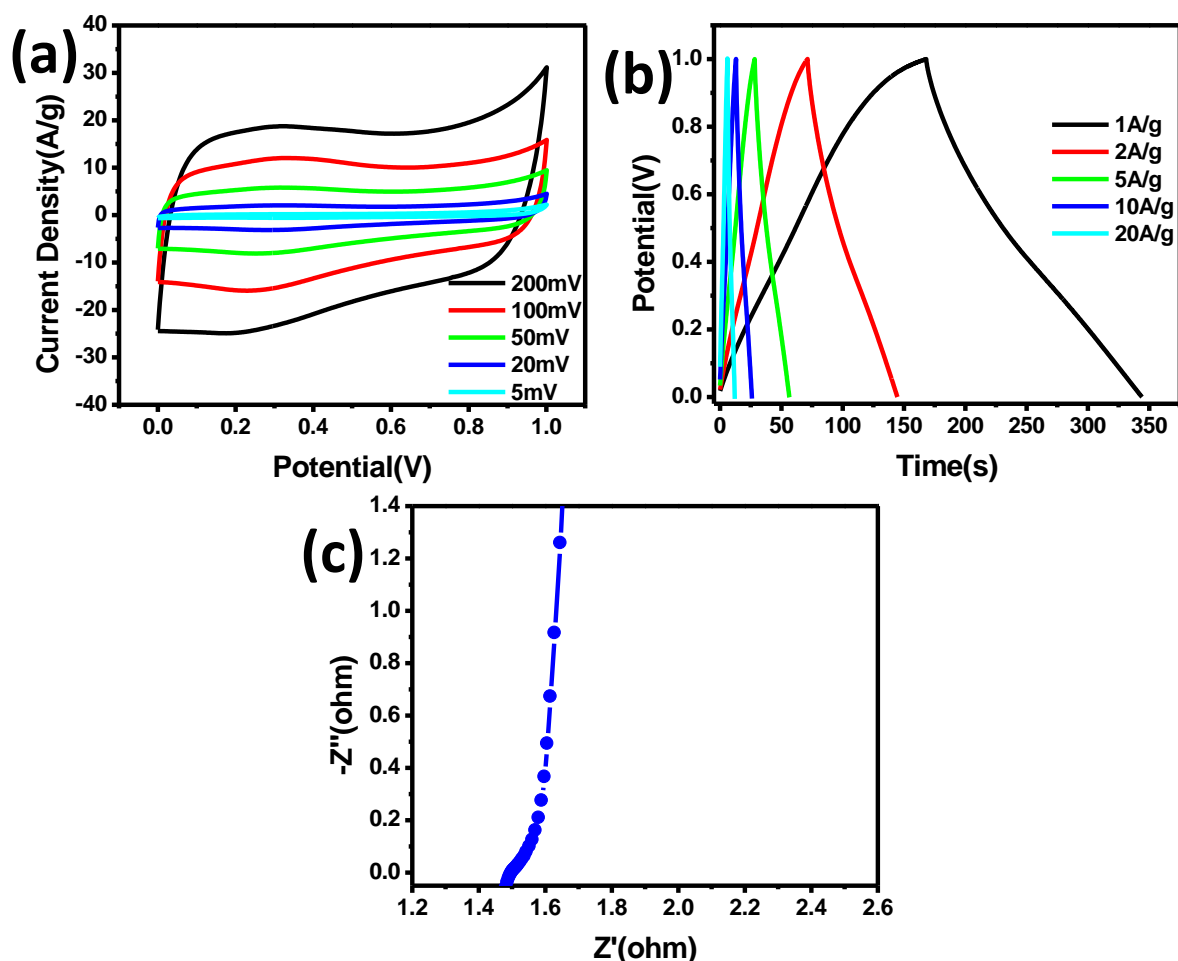


Figure 17: electrochemical performance of pectin derived carbon by template method. a) CV at different scan rates, b) charge-discharge at different current rates, c) Nyquist plot.

Charge discharge plots (figure 17b) also show the triangle shape of charge and discharge curves pointing to ideal capacitor behaviour. Capacitance values of 180F/g at current density 1A/g, 150F/g at 2A/g, 140F/g at 5A/g, 130F/g at 10A/g and 120F/g at 20A/g calculated from charge discharge curves in figure 17b. Impedance Nyquist plot shows the ESR of 1.46 Ω reflecting higher conductivity with vertical region in low frequency carbon corresponding to ideal EDLC capacitor. The ESR of 1.46 Ω is comparable to most of the supercapacitor materials reported and capacitance values are also worth mentioning.

4.3.4 Conclusion

We synthesized electrochemically efficient carbon from cheap and easily available natural precursor pectin by physical pore generation method utilising silica nano particles as a template. The material offers a capacitance of 180F/g at current density of 1 A/g and surface area of 837 m²/g which can be considered good as the precursor being from a natural source.

5. References

1. Rolf, E., *Understanding of Material Science*. 2nd Edition ed.; Springer: **2004**.
2. Dowling, A., et al., *Nanoscience and nanotechnologies: opportunities and uncertainties*, A Report by The Royal Society & The Royal Academy of Engineering, London, July **2004**.
3. C. P. Poole, Jr., F. J. Owens, *Introduction to Nanotechnology*, *Wiley-Interscience*, Hoboken, NJ, **2003**.
4. Lieber, C.M.; "Nanoscale science and technology: Building a big future from small things". *MRS Bull* **2003**, 28, 486-491.
5. Mulkens, J., McClay, J. A., Tirri, B. A., Brunotte, M., Mecking, B. & Jasper, H. Optical lithography solutions for sub-65-nm semiconductor devices. *Proc. SPIE-Int. soc. Opt. Eng.* **2003**, 5040, 753-762.
6. Roscher, M. A.; Vetter, J.; Sauer, D. U., Cathode material influence on the power capability and utilizable capacity of next generation lithium-ion batteries. *Journal of Power Sources* **2010**, 195 (12), 3922-3927.
7. Dresselhaus, M. S.; Thomas, I. L., Alternative energy technologies. *Nature* **2001**, 414 (6861), 332-337.
8. Conway, B. E., *Electrochemical Supercapacitors*. Plenum Publishers: USA, **1999**.
9. Simon, P.; Gogotsi, Y., Materials for electrochemical capacitors. *Nat Mater* **2008**, 7 (11), 845-854.
10. Winter, M.; Brodd, R. J., What Are Batteries, Fuel Cells, and Supercapacitors? *Chemical Reviews* **2004**, 104 (10), 4245-4270.
11. Halper, M. S.; J. C. E., Supercapacitors: A Brief Overview. *The MITRE Corporation, McLean, Virginia, USA*, **2006**, 41.
12. Kötz, R.; Carlen, M., Principles and applications of electrochemical capacitors. *Electrochimica Acta*, **2000**, 45 (15–16), 2483-2498.
13. Liu, C.; Li, F.; Ma, L. P.; Cheng, H. M.; Advanced Materials for Energy Storage. *Adv. Mater.***2010**, 22, E28-E62.

14. Zhang, L. L. and Zhao, X.S., Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **2009**, *38*, 2520-2531.
15. Bose, S.; Kuila, T.; Mishra, A.K.; Rajashekhar, R.; Kim, N.H. and Lee, J.H., Carbon-based nanostructured materials and their composites as supercapacitor electrodes. *J. Mater. Chem.* **2012**, *22*, 767-784.
16. Jiang, H.; Ma, J. and Li, C.Z., Mesoporous carbon incorporated metal oxides nanomaterials as supercapacitor electrodes. *Adv. Mater.* **2012**, *24*, 4197-4202.
17. Lu, X.H.; Zhai, T.; Zhang, X.H.; Shen, Y.Q.; Yuan, L.Y.; Hu, B.; Gong, L.; Chen, J.; Zhou, J.; Tong, Y.X.; Wang, Z.L., WO₃-x@Au@MnO₂ Core-Shell Nanowires on Carbon Fabric for High-Performance Flexible Supercapacitors. *Adv. Mater.* **2012**, *24*, 938-944.
18. Wang, B.; Chen, J.S.; Wang, Z.Y.; Madhavi, S.; Lou, X.W., Green Synthesis of NiO Nanobelts with Exceptional Pseudo-Capacitive Properties. *Adv. Energy Mater.*, **2012**, *10*, 1188.
19. Wei, T.Y.; Chen, C.H.; Chien, H.C.; Lu, S.Y.; Hu, C.C., A Cost-Effective Supercapacitor Material of Ultrahigh Specific Capacitances: Spinel Nickel Cobaltite Aerogels from an Epoxide-Driven Sol-Gel Process. *Adv. Mater.*, **2010**, *22*, 347.
20. Deprez, N. and McLachlan, D. S., The analysis of the electrical conductivity of graphite conductivity of graphite powders during compaction. *J. Phys. D: Appl. Phys.* **1988**, *21*, 101.
21. Frackowiak, E., Carbon materials for supercapacitor application. *Phys. Chem. Chem. Phys.*, **2007**, *9*, 1774-1785.
22. Zhai, Y.; Dou, Y.; Zhao, D.; Fulvio, P.F.; Mayes, R.T. and Dai, S., Carbon Materials for Chemical Capacitive Energy Storage. *Advanced Materials*, **2011**, *23*, 4828-4850.
23. Huang, J.; Sumpter, B.G., and V. Meunier, V., A Universal Model for Nanoporous Carbon Supercapacitors Applicable to Diverse Pore Regimes, Carbon Materials, and Electrolytes. *Chem.-A Eur. J.*, **2008**, *14*, 6614-6626.
24. Hulicova-Jurcakova, D.; M. Seredych, M.; G. Q. Lu, G.Q., and Bandosz, T.J., Combined effect of nitrogen- and oxygen-containing functional groups of

microporous activated carbon on its electrochemical performance in supercapacitors. *Adv. Funct. Mater*, **2009**, *19*, 438–447.

25. Cohen, N., and M. S. Silverstein, M.S., Porous Carbon Monoliths from Emulsion-Templated Polyacrylonitrile. *Polymer*, **2011**, *52*, 282–287.

26. Chen, X.Y.; Chen, C.; Zhang, Z.J., and Xie, D.H., nitrogen-doped porous carbon spheres derived from polyacrylamide. *Ind. Eng. Chem. Res.*, **2013**, *52*, 12025–12031.

27. Morishita, T.; Soneda, Y.; Tsumura, T., and Inagaki, M., Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors. *Carbon*, 2006, *44*, 2360–2367.

28. Wei, L.; Sevilla, M.; Fuertes, A. B.; Mokaya, R., and Yushin, G., Polypyrrole-Derived Activated Carbons for High-Performance Electrical Double-Layer Capacitors with Ionic Liquid Electrolyte. *Adv. Funct. Mater*, **2012**, *22*, 827–834.

29. Qian, W.; Sun, F.; Xu, Y.; Qiu, L.; Liu, C.; Wang, S., and Yan, F., Human Hair-Derived Carbon Flakes for Electrochemical Supercapacitors. *Energy Environ. Sci.*, **2014**, *7*, 379–386.

30. Wu, X. L.; Wen, T.; Guo, H. L.; Yang, S.; Wang, X. K., and Xu, A. W., Biomass-Derived Sponge-like Carbonaceous Hydrogels and Aerogels for Supercapacitors. *ACS Nano*, **2013**, *7*, 3589–3597.

31. Rolison, D. R.; Long, J. W.; Lytle, J. C.; Fischer, A. E.; Rhodes, C.P.; McEvoy, T. M.; Bourg, M. E., and Lubers, A. M., Multifunctional 3D nanoarchitectures for energy storage and conversion. *Chem. Soc. Rev.*, 2009, *38*, 226–252.

32. Lee, Y. J.; Jung, J. C.; Park, S.; Seo, J. G.; Baeck, S. H.; Yoon, J. R.; Yi, J., and I. K. Song, I. K.; Preparation and characterization of metal-doped carbon aerogel for supercapacitor *Current Appl. Phys.*, **2010**, *10*, 947–951.

33. Nata, I. F.; Wang, S. S. S.; Wu, T. S. and Lee, C. K., Carbonaceous hydrogels based on hydrothermal carbonization of glucose with chitin nanofibers. *Soft Matter*, **2012**, *8*, 3522–3525.

35. Friedrich W, Knipping P, von Laue M. "Interferenz-Erscheinungen bei Röntgenstrahlen". *Sitzungsberichte der Mathematisch-Physikalischen Classe der Königlich-Bayerischen Akademie der Wissenschaften zu München* **1912**, 303

36. Bragg WL (1912). "The Specular Reflexion of X-rays". *Nature* **90**, 410, 2250.

37. Gardiner, D.J.; *Practical Raman spectroscopy*, **1989**.
38. A. B. Fuertes and M. Sevilla, *ACS Applied Materials & Interfaces*, 2015, **7**, 4344-4353.
39. D. Puthusseri, V. Aravindan, B. Anothumakkool, S. Kurungot, S. Madhavi and S. Ogale, *Small*, 2014, **10**, 4395-4402.
40. W. Qian, F. Sun, Y. Xu, L. Qiu, C. Liu, S. Wang and F. Yan, *Energy & Environmental Science*, **2013**, **7**, 379-386.
41. M. Wahid, G. Parte, D. Phase and S. Ogale, Yogurt: a novel precursor for heavily nitrogen doped supercapacitor carbon. *Journal of Materials Chemistry A*, **2014**, **3**, 1208-1215.
42. M. Wahid, D. Puthusseri, D. Phase and S. Ogale, *Energy & Fuels*, **2014**, **28**, 4233-4240.
43. J. Wang and S. Kaskel, *Journal of Materials Chemistry*, 2012, **22**, 23710-23725.
44. L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya and G. Yushin, *Advanced Functional Materials*, 2011, **22**, 827-834.
45. Y. S. Yun, S. Y. Cho, J. Shim, B. H. Kim, S.-J. Chang, S. J. Baek, Y. S. Huh, Y. Tak, Y. W. Park, S. Park and H.-J. Jin. Microporous Carbon Nanoplates from Regenerated Silk Proteins for Supercapacitors. *Advanced Materials*, **2013**, **25**, 1993-1998.
46. W. Sun, R. Zheng and X. Chen, *J. Power Sources*, **2010**, **195**, 7120.
47. L. Cui, J. Li and X. G. Zhang, *J. Appl. Electrochem.*, **2009**, **39**, 1871.
48. R. Ryoo, S. H. Joo and S. Jun, *The Journal of Physical Chemistry B*, **1999**, **103**, 7743-7746.
49. Q. Shi, R. Zhang, Y. Lv, Y. Deng, A. A. Elzatahrya and D. Zhao, *Carbon*, **2014**, **84**, 335-346.
50. S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, **2001**, **412**, 169-172.
51. M.-S. Kim, B. Fang, J.H. Kim, D. Yang, Y.K. Kim, T.S. Bae, J.-S. Yu, *J. Mater. Chem.* **2001**, **21**, 19362-19367.
52. Frackowiak, E. and Beguin, F.; *Carbon*, **2001**, **39**, 937.
53. J. Gamby, P. L. Taberna, P. Simon, J. F. Fauvarque and M. Chesneau, *J. Power Sources* **2001**, **101**, 109.