3

Materials and Methods

3.1. Introduction

Porous carbon is an extensively investigated electrode material for supercapacitors owing to its high specific surface area and excellent chemical and thermal stabilities. Several researchers have attained better electrochemical performances in the preparation of carbon from bio-mass materials such as pinecone, pineapple leaves, coconut shell, groundnut shell etc., due to its unique morphology, hierarchical structure and heteroatoms (O, N, P or S). Also, spinel structured $ZnCo_2O_4$ is a potential electrode material having high theoretical capacitance (2604 Fg^{-1}) with multiple oxidation states. The different morphologies of spinel structured $ZnCo_2O_4$ (Zinc cobaltite) have been prepared by the researchers via hydrothermal, solvothermal, co-precipitation etc. In this Chapter, preparation of carbon from *Prosopis juliflora* biomass precursor by conventional heating method and plasma firing and $ZnCo_2O_4$ by sol-gel method are discussed. Systematic analysis is conducted on the prepared carbon and spinel structured $ZnCo_2O_4$ material to have complete understanding on the material. Further, the method of electrode preparation and device assembly have also been demonstrated for supercapacitor applications. Further, the prepared materials are assembled into symmetric and asymmetric devices and the electrochemical performances are evaluated. The materials and methods involved are presented in this Chapter.

3.2. Chemicals/materials used

Table 4 - List of chemicals used

S. No	Materials	Chemical Formula	Brand	Purity (%)
1.	Zinc Chloride dry	$ZnCl_2$	Merck	>98
2.	Cobalt (III) chloride hexahydrate	$CoCl_2.6H_2O$	Merck	≥98
3.	Nickel (II) chloride hexahydrate	$NiCl_2.6H_2O$	Merck	≥98
4.	Chromium (III) chloride hexahydrate	$CrCl_2.6H_2O$	Sigma aldrich	≥98
5.	Iron (III) chloride	$FeCl_3$	Merck	>98

S. No	Materials	Chemical Formula	Brand	Purity (%)
6.	Potassium Hydroxide pellets	KOH	Merck	≥84
7.	Sulfuric acid	H_2SO_4	Merck	95-98
8.	Acetone	C_3H_6O	Merck	≥ 99
9.	Citric acid	$C_6H_8O_7$	Merck	≥ 99
10.	Ethanol	C_6H_5OH	china	
11.	n-Methyl-2-Pyrrolidone	C_5H_9NO	Sigma-Aldrich	99.9
12.	Poly(Vinylidene Fluoride)	$(-CH_2CF_2-)_n$	Sigma-Aldrich	99.9
13.	Polyvinyl Alcohol	PVA	Himedia	degree of hydrolysis 86.50–89.00
14.	Cellulose acetate filter paper	-	Whatmann	>98
15.	Copper foil	Cu	Sigma aldrich	≥99
16.	Carbon black	C	Alfa Aesar	≥99.9
17.	Silver paste	Ag	Sigma-Aldrich	>99

Using the listed chemicals, the following materials are prepared in this work for device fabrication.

Table 5 - List of electrode materials prepared

Material	Preparation Method	Purpose
Carbon from bark of *P. juliflora* (B-Carbon)	Conventional heating method	Anode
Carbon from Stick of *P. juliflora* (S-Carbon)	Conventional heating method	
Carbon from bark of *P. juliflora* (PB-Carbon)	Plasma firing	
$ZnCo_2O_4$	Sol-gel	Cathode
Fe, Cr: $ZnCo_2O_4$	Sol-gel	
Ni, Cr: $ZnCo_2O_4$	Sol-gel	

3.3. Synthesis of Carbon by Conventional Heating Method

The synthesis procedure for carbon from biomass is as follows: pre-carbonization, activation and followed by post carbonization. In the present case, biomass (stick/bark of *P. juliflora*) is washed with distilled water to remove any impurities. Then, the material is dried and ground into a fine powder. It is preactivated with activating agent 1M H_2SO_4 for 24 hrs. After 24 hrs, the product is washed several times with distilled water and ethanol in order to remove activating agents from the precursors. Then, resultant product is heated at 800°C for 2 hrs and again it is heated at same temperature and duration. A schematic diagram of this method of preparation is shown in Figure 4. The conventional heating method has several advantages, including low cost, low temperature, higher yield, short activation time, and higher porosity development with high surface area. The process is claimed in Intellectual Property Rights.

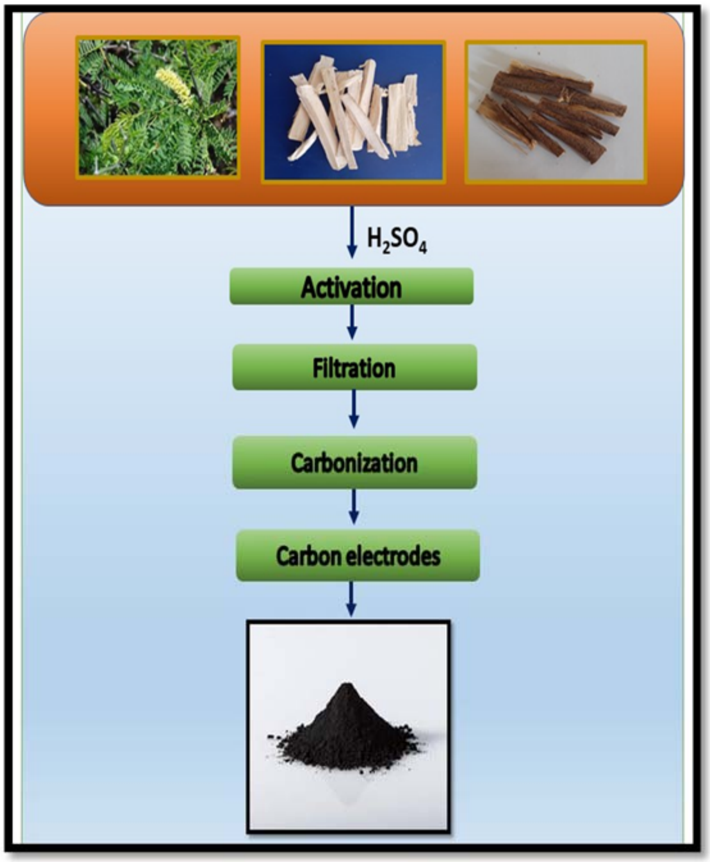

Figure 4 - Pictorial flowchart for the preparation of carbon

3.4. Plasma firing method

In this method, the bark of *P. juliflora* is collected, washed with plenty of distilled water and dried. Then, dried sample is ground into powder. It is converted into pellets of 12 mm under 12 Mpa pressure using pelletizer. The prepared pellets are treated by plasma source with an applied power of 1.248 KW for 2 mins. Then the product is collected from the crucible. The plasma treatment method has several advantages, such as low cost, rapid, no activation and no chemicals involved.

3.5. Sol-gel method

In sol-gel process, the products are converted into colloids using chelating agents. The powder is formed when processing the gel-like solution at a particular temperature. This method of preparation provides advantages like controlled morphology, particle size and microstructure while maintaining the pH value of the solution. As a result, even minor changes in the reaction process might have a major impact on the nature of the products. This approach is particularly beneficial for systems with high melting points. In this study, the highly crystalline electrode material, Zinc cobaltite ($ZnCo_2O_4$) has been prepared using the sol-gel process. Figure 5 depicts the preparation technique in detail. This procedure is adopted for preparing the pristine Zinc cobaltite material.

A 1 M solution of Zinc chloride anhydrous and 2 M solution of cobalt chloride hexahydrate ($CoCl_2.6H_2O$) are weighed in appropriate ratio and mixed together in distilled water. The 1.33 M citric acid solution is prepared and poured into the already prepared chloride solution under continuous stirring until all the salts completely get dissolved entirely. The resultant solution is heated at 80°C for 6h to achieve the gel formation and then calcined at 550°C for 5h after which the powder is collected for analysis.

In the preparation of doped samples, corresponding metal chlorides of dopants have been weighed and added to the parent metal chloride solution. The Ni and Cr doped Zinc cobaltite is prepared by the addition of 0.1 M solution of chromium chloride hexahydrate ($CrCl_2.6H_2O$), 0.1 M solution of nickel chloride hexahydrate ($NiCl_2.6H_2O$) into the 0.8 M solution of $ZnCl_2$ and 2 M solution of $CoCl_2.6H_2O$ and the rest of the procedures are similar to the pristine sample prepared, as shown in Figure 5.

In the preparation of Fe and Cr doped Zinc cobaltite, 0.1M solution of chromium chloride hexahydrate ($CrCl_2.6H_2O$) and 0.1M solution of iron chloride ($FeCl_3$) are added into 0.8M solution of Zinc chloride ($ZnCl_2$). Then, similar procedure is followed as mentioned in the pure Zinc cobaltite. The prepared samples are characterized for structural, morphological, and electrochemical analysis are made.

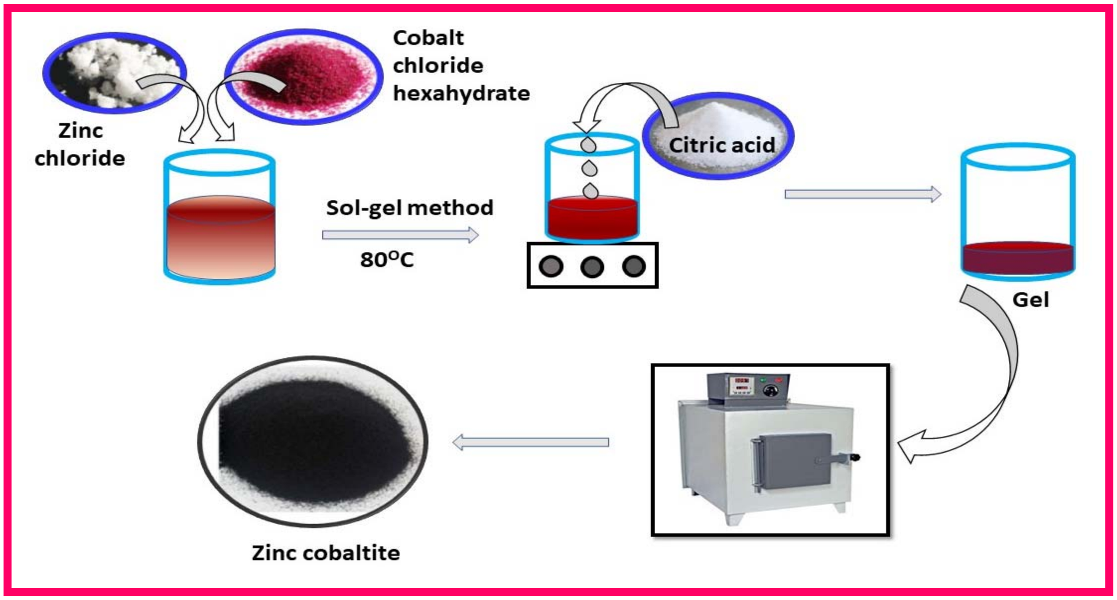

Figure 5 - Pictorial flowchart for the preparation of Zinc cobaltite

3.6. Characterization of prepared material:

3.6.1. Structural Characterization

3.6.1.1. X-Ray Diffraction

The structural phases of all the prepared materials have been verified using the X-ray diffraction technique (X' Pert Pro PAN analytical instrument with a CuKα radiation). The XRD is a versatile and rapid method for determination of the several structural parameters including crystallite size, unit cell dimensions and inter-planar distance of as-prepared crystalline samples.

Rietveld refinement

To ensure the phase formation or occurrence of secondary phases in pristine Zinc cobaltite/ doped Zinc cobaltite, Rietveld refinement has been employed. In the present work, Rietveld refinement has been performed by GSAS- II software with the help of structure file (.cif) obtained from COD (crystallography open database). The COD-ID of cif file is 5910136 which has the space group of $Fd\bar{3}m$ and lattice parameter of 8.1□. The visualized structure of as-prepared Zinc cobaltite materials is visualized from refined cif file using VESTA software.

3.6.1.2. Raman Spectroscopy

Raman analysis is carried out for all the prepared carbon and metal cobaltite materials. The Raman spectrum is recorded in range between 100-1000 cm^{-1} using LabRAM High Resolution 800 UV Confocal Raman microscope and green laser (He-Ne 532.14 nm) is used as an excitation source.

3.6.1.3. Field Emission Scanning Electron Microscopy

Surface morphological features of all the prepared samples have been analysed by Field Emission Scanning Electron Microscopy with help of TESCAN MIRAC3 and Carl Zeiss (USA) instrument.

3.6.1.4. Transmission Electron Microscopy

TEM analysis (Instrument make: Thermofisher and Model: Talos F200 S) has been used to analyse the particles or range of ordering with higher magnification and clarity on morphology for the carbon samples.

3.6.1.5. Elemental Analysis

Phase purity and presence of impurity elements in the prepared carbon and Zinc cobaltite electrode materials have been evaluated by EDX analysis. In the present thesis, EDX study has been performed using annexed with (Quantax EDS detector instruments) TESCAN MIRAC3, Carl Zeiss (USA) FESEM instruments.

3.6.1.6. Surface Area Analysis

The surface area of prepared carbon materials is measured through BET isotherms using Quantachrome NOVA instrument. Also, the existence of meso-pores and micro-pores in as-synthesized materials are determined via N_2 adsorption/desorption isotherm.

3.7. Working Electrode Preparation

The working electrodes are prepared by mixing 85 wt.% of active materials, 10 wt.% of conductive carbon black, 5 wt.% of polyvinyl dimethyl fluoride (PVdF) as a binder and N-methyl 2-pyrrolidone (NMP) as a solvent. The homogeneous slurry is obtained after thorough mixing of the materials with adequate solvent. The resultant slurry is coated on the copper foil by doctorblade method manually, which acts as a current collector, followed by drying at 80°C for 6 h to ensure the complete evaporation of NMP. Then, the coated electrode is cut into desirable dimensions (1x1 cm^2 for material characterizations and 2x2 cm^2 for device characterizations) and used for performance testing. Figure 6 shows the preparation procedure of working electrode.

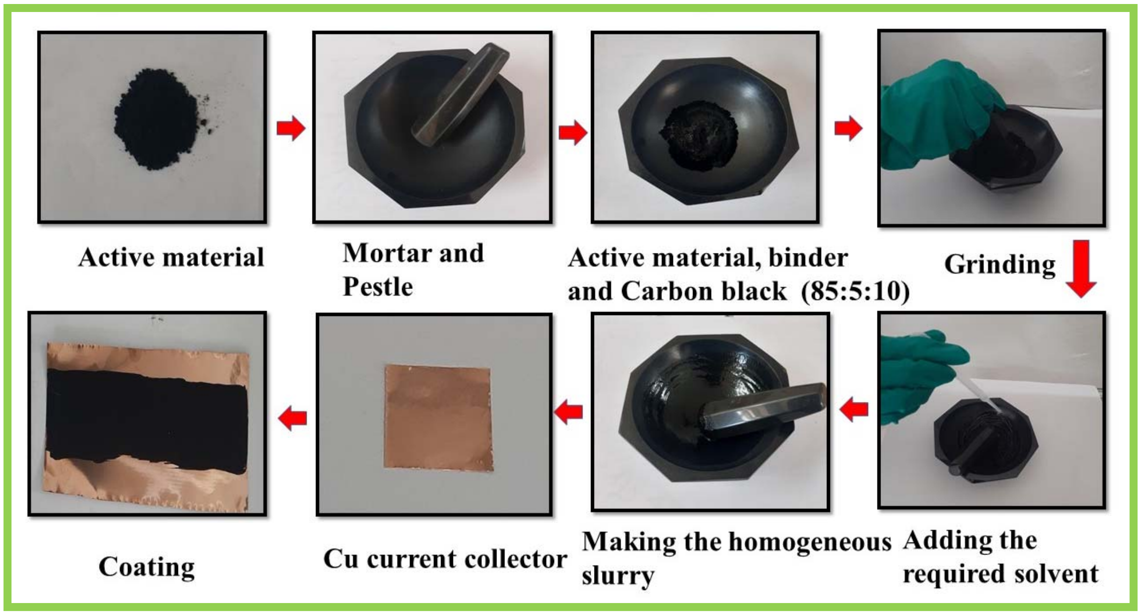

Figure 6 - Pictorial flowchart for the preparation of working electrodes

3.8. Device assembly

In this research work, devices are fabricated in two modes: i) symmetric mode and ii) asymmetric mode. In symmetric configuration, similar electrodes are used in either side of the PVA – KOH electrolyte. In asymmetric device configuration two different materials are used. However, in both the configurations gel polymer electrolyte is used. The PVA-KOH is prepared by dispersing PVA (1g) and KOH (1g) in 20 ml distilled water. After thorough mixing, the gel is formed and used as an electrolyte for the supercapacitor device.

For holding of electrolyte, a separator, Whatman filter paper (Cat. No. 1001-110) (pore size ~11 µm; 0.18 mm thickness) is chosen and by immersing it in the prepared gel polymer electrolyte for 1 min electrolyte is made ready for assembly. Figure 7 represents the steps involved in the supercapacitor device assembly.

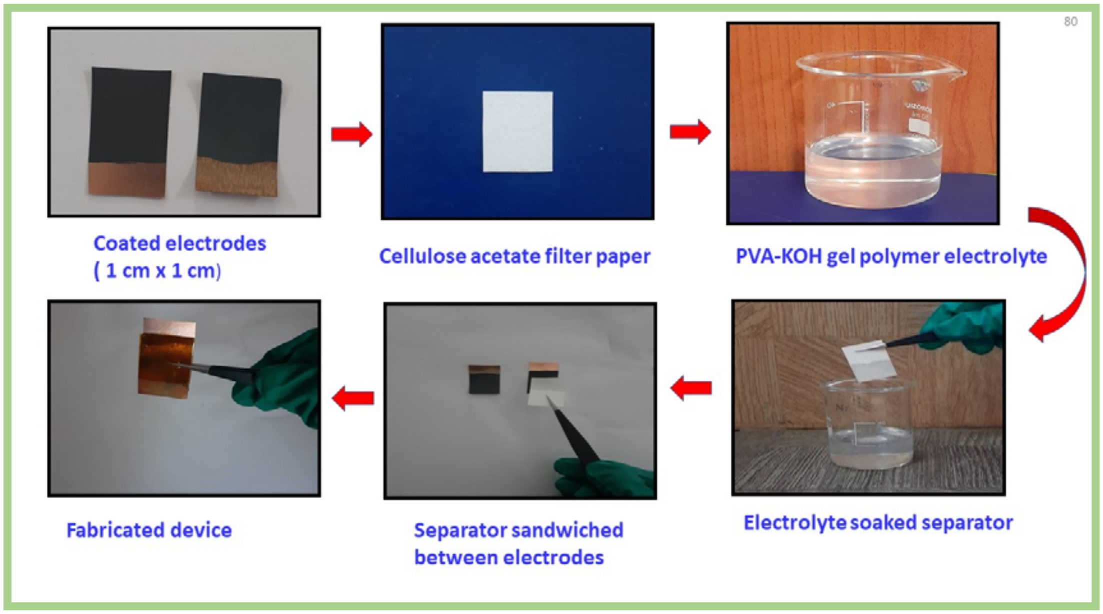

Figure 7 - Pictorial flowchart for the device assembly

Table 6 - List of assembled all solid-state supercapacitor

Device assembly	Type
S-Carbon /PVA-KOH/ S-Carbon	Symmetric
B-Carbon/PVA-KOH/B-Carbon	
PB-Carbon/PVA-KOH/PB-Carbon	
$ZnCo_2O_4$/PVA-KOH/$ZnCo_2O_4$	
Fe, Cr: $ZnCo_2O_4$/PVA-KOH/Fe, Cr: $ZnCo_2O_4$	
Ni, Cr: $ZnCo_2O_4$/PVA-KOH/Ni, Cr: $ZnCo_2O_4$	
S-Carbon /PVA-KOH/$ZnCo_2O_4$	Asymmetric (Anode/electrolyte/cathode)
S-Carbon /PVA-KOH/Fe, Cr: $ZnCo_2O_4$	
S-Carbon /PVA-KOH/ Ni, Cr: $ZnCo_2O_4$	
B-Carbon /PVA-KOH/$ZnCo_2O_4$	
B-Carbon /PVA-KOH/Fe, Cr: $ZnCo_2O_4$	
B-Carbon /PVA-KOH/ Ni, Cr: $ZnCo_2O_4$	
PB-Carbon/PVA-KOH/$ZnCo_2O_4$	
PB-Carbon /PVA-KOH/Fe, Cr: $ZnCo_2O_4$	
PB-Carbon/PVA-KOH/ Ni, Cr: $ZnCo_2O_4$	

3.8.1. Electrochemical Characterizations

A wide range of equipment and methodologies have been developed for the electrochemical characterization of supercapacitors. Cyclic voltammetry (CV) and Galvanostatic charge/discharge (GCD) testing are two of the most often employed methods. Both the techniques measure the three fundamental parameters such as voltage, current, and time, and additional metrics like capacitance can be determined from them. For basic analysis, a three-electrode setup with a working electrode, counter electrode, and reference electrode is utilised. Figure 8 depicts the schematic of electrode setup. The three-electrode setup allows to examine the performance of working electrode. Throughout the experiment, the reference electrode maintains a constant potential of the working electrode. The circuit is completed by the counter electrode, which does not interfere with the working electrode's reaction.

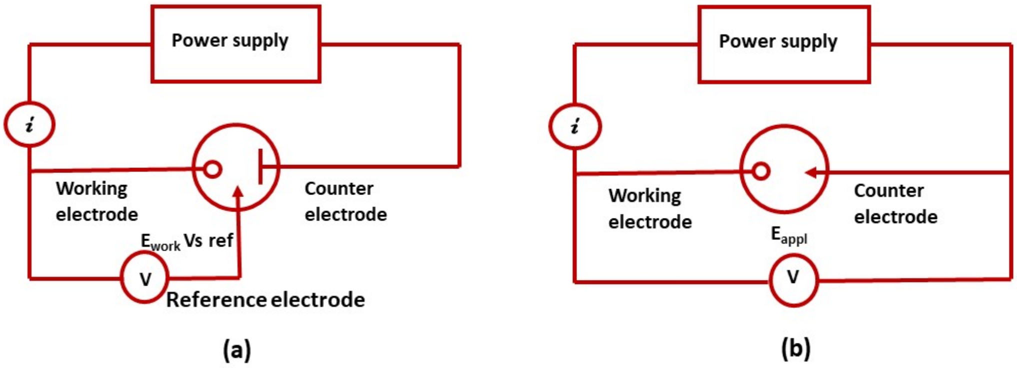

Figure 8 - The schematic of electrode setup: (a) Three electrode configuration and (b) two electrode configuration

3.8.2. Cyclic Voltammetry (CV)

In cyclic voltammetry analysis, the potential is applied between two limitations of the working electrode, called as potential windows or operating potentials. The potential of the working electrode is swept at the constant scan rate. The value of the current generated in the electrochemical system is recorded as a function of the applied potential during positive and negative scans. The mechanism of energy storage at the electrode/electrolyte interface is attributed to the shape of the CV profile. Ideal capacitors possess unique rectangular shape as the potential is changed linearly. Batteries exhibit reversible redox processes which induce faradaic peaks in the voltammogram. Due to the presence of redox peaks, pseudo-capacitors have a quasi-rectangular shape.

The specific capacitance of a material is calculated from CV using the formula

$$\boldsymbol{C = \frac{\int IdV}{vmV}} \qquad \textbf{(Fg}^{\mathbf{-1}}\textbf{)} \qquad \textbf{(1)}$$

where,

$\int IdV$ – integral area of the curve (A.V)

v- scan rate (mV/s),

m-mass of the active material (g),

V-potential window (V).

3.8.3. Galvanostatic Charge-Discharge Analysis

The galvanostatic charge/discharge (GCD) cycling is a process of charging and discharging the working electrode at a constant current. When a constant current is applied, charges are stored at the interface of electrode/electrolyte, resulting in a potential change over time. The electrode is then discharged with a negative current. According to constant current, the change in potential and time is measured. The investigation of voltage versus time kinetics with constant current provides the electrochemical properties of working electrode.

The equation for calculating the specific capacitance from the GCD curve is

$$\boldsymbol{C = \frac{I\Delta t}{m\Delta V}} \qquad \textbf{Fg}^{\mathbf{-1}} \qquad \textbf{(2)}$$

The areal capacitance is calculated by the formula:

$$\boldsymbol{C = \frac{I\Delta t}{A\Delta V}} \qquad \textbf{mF/cm}^{\mathbf{2}} \qquad \textbf{(3)}$$

where,

I– discharge current (A),

Δt- discharge time (s)

ΔV- potential window (V)

For non-linear GCD curves, the specific capacitance is elucidated with well know relation:

$$\mathbf{C} = \frac{2I\int Vdt}{mV^2 \,|_{Vi}^{Vf}} \quad \mathbf{Fg^{-1}} \tag{4}$$

The areal capacitance is determined by the equation:

$$C_A = \frac{2I\int Vdt}{AV^2 \,|_{Vi}^{Vf}} \ \mathbf{mF/cm^2} \tag{5}$$

where,

$\int Vdt$– integral area of the GCD curve

A- area of the electrode (cm^2)

V_f- final voltage (V)

V_i- initial voltage (V)

The energy density (E) and power density (P) of the device is calculated by the following equations:

$$E = \frac{1}{2} \mathrm{C}\, \Delta \mathrm{V}^2 \qquad \mathbf{WhKg^{-1}} \tag{6}$$

$$P = \frac{\mathrm{E}}{\Delta \mathrm{t}} \qquad \mathbf{WKg^{-1}} \tag{7}$$

The areal energy and power density is elucidated by the following equations:

$$E_A = \frac{1}{2} C_A\, \Delta \mathrm{V}^2 \qquad \mathbf{\mu Wh/cm^2} \tag{8}$$

$$P_A = \frac{E_A}{\Delta \mathrm{t}} \qquad \mathbf{\mu W/cm^2} \tag{9}$$

3.8.4. Electrochemical Impedance Spectroscopy

The exploration of redox reaction mechanisms, charge transfer resistance and electrical response of the carbon, pure and doped Zinc cobaltite are determined by EIS analysis. All the electrochemical studies are carried out with help of Bio-logic SP-150 also the internal resistance, capacitive, and resistive components of assembled device is studied by analysing before and after cycling in three electrode system and two electrode device assembly and each of three electrode system and two electrode assembled devices.

Fitting data by software

The obtained impedance data for all the as-prepared materials have been fitted using EC-Lab software and corresponding equivalent circuit is generated of each three electrode system and two electrode assembled devices and given in the respective result and discussions sections. The electrochemical performance of present work has been performed by three electrode system with use of 1M KOH aqueous electrolyte. The Pt and Ag/AgCl is employed as counter and reference electrode respectively.

3.9. Summary

The preparation methods of carbon from biomass *Prosopsis juliflora* bark and stick are discussed. The structural characterization is done with XRD, RAMAN, and surface analysis is by BET. The device assembly details are given in detail. Electrochemical analysis and the details of how the analysis is made is elaborated in this Chapter.