Introduction

1.1 Introduction

The present day scenario of renewable energy production has taken over energy storage infrastructure creating hurdle in bringing the carbon reduction which is essentially awaited one for the globe. The battery evolution faces challenge of scarcity for high quality graphene in larger scale. Current production costs are excessively expensive making battery productions of required quantum a nearly impossible one. The limitations of fast charging connected to the thermal runaway in batteries in terms of safety drives the supercapacitors more important replacing the car batteries with quick charging and thermally stable energy storage devices. End of December 2021, “First Graphene” has announced a milestone achievement of specific capacitance of 140 Fg^{-1} while activated carbon cells typically having 35 Fg^{-1}. “Log Materials” a Bangalore based EV battery manufacturing has said about the challenges with local unavailability of battery grade raw materials and reduced functioning of graphite industries on environmental aspects possess grand challenge on the energy storage growth. Hence, the present work of obtaining graphitic/crystalline carbon through biomass and utilization of less toxic oxides and device fabrication with low cost materials with simple technique would be the need of the hour which has been attempted here.

1.2. Supercapacitors

Supercapacitors (SCs), otherwise called as “electrochemical capacitors” (ECs), are the devices for energy storage owing to its unique features. It possess fast charge and discharge reversible cycles. They deliver a higher specific capacitance (in terms of Farad/gram) and energy density (10 Wh Kg^{-1}) than traditional capacitors and a higher power density (around 10^5 W Kg^{-1}) than batteries **(Zhang & Zhao, 2009)**. Supercapacitors are one of the most fascinating new breakthroughs among the world of energy storage devices when compared to batteries.

SCs with high power density, longer cycle-life and moderate energy density are the potential candidates due to their facile route to storing energy efficiently in portable electronic devices, namely hybrid vehicles, electronic devices, memory backup systems, military devices and energy harvesting applications etc. But the low energy density of the supercapacitors has the major barrier to their extensive use in practical applications. For a long time, energy density has been restricted to levels much below 10 Wh Kg^{-1}**.** Hence, the researchers have focussed on achieving the high energy density supercapacitors.

The world of supercapacitor still needs to be explored to understand the performance factors of this device and examine the contribution of different materials as supercapacitor components towards betterment of the existing technology. In general, SCs consists of two electrodes that are coated on current collectors and separator soaked with an electrolyte in between the two electrodes. The energy has been stored by the separation of electric charge accumulated on the surface of the electrodes, as shown in Figure 1. Becker, General Electric introduced the theory of SCs for the first time in 1957. Robert A. Rightmire, his fellow researcher at the Standard Oil Company of Ohio improved it in the 1960s. Maxwell Technologies, Panasonic, Nippon Chemi-Con, etc. are the key concerns manufacturing supercapacitors. Some of the major manufacturer of SC and their performance is listed in Table 1 **(Sharma & Bhatti, 2010)**.

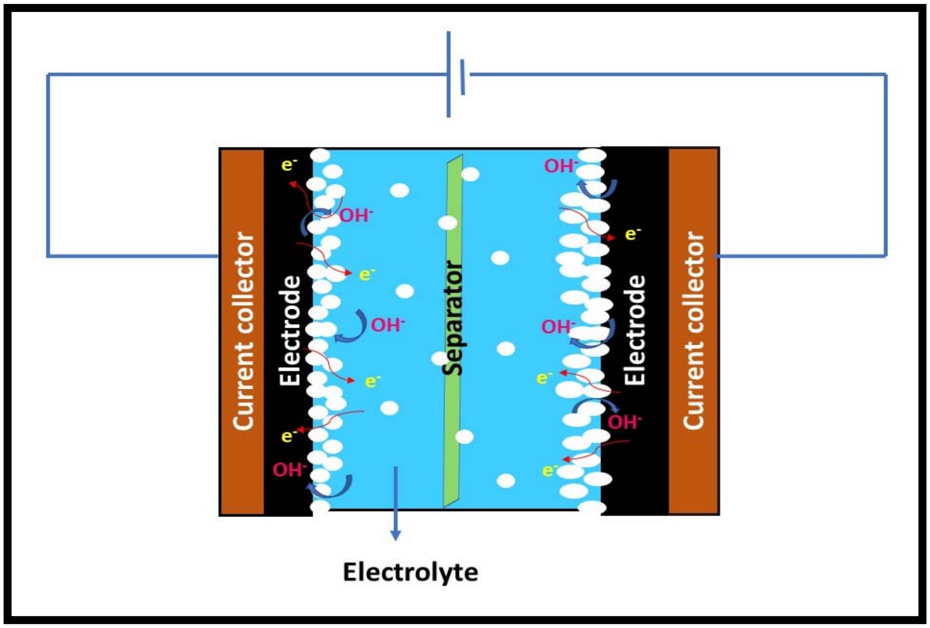

Figure 1 - Configuration of Supercapacitor

Table 1 - Features of commercial Supercapacitor and their manufacturers

Organization	Nomenclature	Potential window (V)	Capacitance (F)
Cap XX – Tecate	Super Capacitor	2.25–4.5	0.09–2.8
Copper	Power stor	2.5–5.0	0.47–50
ELNA Mouser India	Dyna cap	2.5–6.8	0.033–100
TDK EPCOS	Ultra-capacitor	2.3–2.5	5–5000
Maxwell Technologies	Boostcap	2.5	1.6–2600
Nesscap	EDLC	2.7	10–5000
Panasonic	Gold capacitor	2.3–5.5	0.1–2000
Kyocera AVX	Bestcap	3.5–12	0.022–0.56
NEC Tokin	Super capacitor	3.5–12	0.01–6.5
SAFT and ESMA	Capacitor modules	12–52	100–8000
Kold Ban International	Kapower	12	1000

1.3. Categories of Supercapacitors

- **Charge Storage Based classification:**

Depending on the charge storage mechanism, three types of supercapacitors can be described.

- **Electrical double layer capacitors** (EDLCs), where the energy storage is due to the formation of an electric double layer at electrode and electrolyte interface. The performance is mainly dependent on the surface area of the electrodes
- **Pseudocapacitors**, the energy is stored by faradic reaction occurred on the surface of the redox-active materials
- **Hybrid capacitors**, store the energy using both Faradaic and non-Faradaic processes. The hybrid system works by combining the use of a double layer electrode with a pseudo-capacitance electrode that is charged in two different modes. Hence, high operating potential window and a lower equivalent series resistance have been achieved which ultimately enhance supercapacitor performance **(Obreja, 2008).**

A hierarchical tree is drawn to understand the classification of supercapacitors as given in Figure 2.

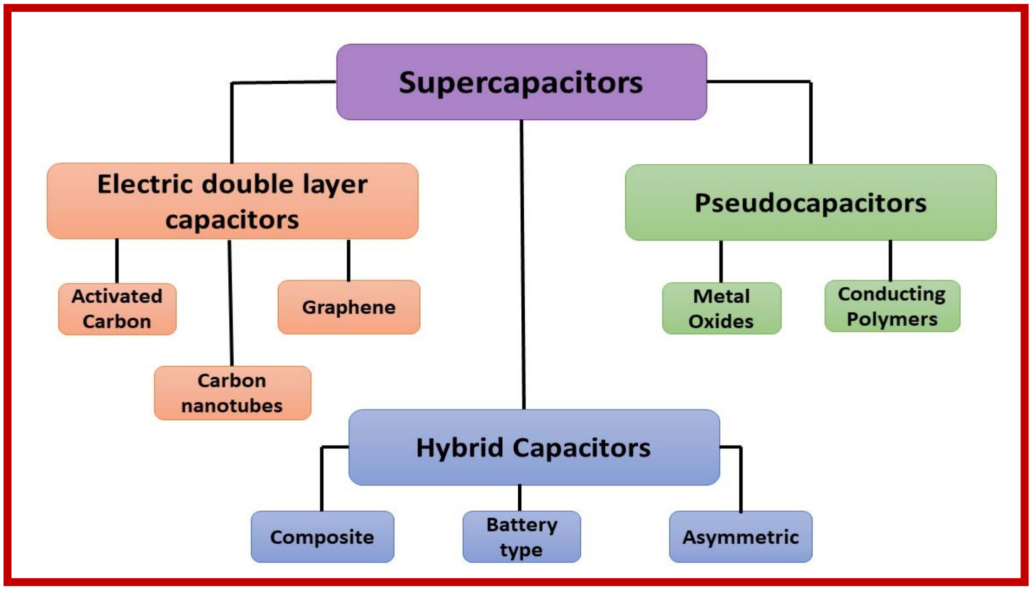

Figure 2 - Classification of Supercapacitors

- **Geometry based classification**

Based on their constructional configuration, supercapacitors are divided into two types.

- **Symmetric supercapacitor:** In symmetric supercapacitor, the two electrodes are made up of the same material and
- **Asymmetric Supercapacitor:** In an asymmetric supercapacitor, the two different materials can be used as an electrode.

For commercialization, generally, symmetric structure has been employed in electric double-layer capacitors (EDLCs), which use carbon-based materials namely activated carbon, carbon nanotubes, graphene-based materials, and carbon aerogels **(Zhang et al., 2011).**

1.3.1. Carbon- based electrodes

Carbon based materials are eternal choice of interest for supercapacitor and battery applications. One of the key benefits of employing carbonaceous materials as an electrode in energy storage system is due to ease of tailoring specific surface area, porous structure, stability and electrical conductivity. Graphene-based materials, carbon nanotubes, activated carbon are commonly used among different forms of available carbon materials. Especially, they are highly suitable for supercapacitor applications owing to their prospective aspects towards the requirements.

1.3.1.1. Graphene

Carbon atoms are linked with each other in a hexagonal honeycomb lattice to make graphene **(Sur, 2012).** It is a widely used material because of its high mechanical strength, thermal and electrical conductivity. Different technologies can be used to prepare high quality graphene on big scale. Graphene is exfoliated from graphite. Again graphite is excavated that demands a cost and incurs lot of environmental pollution. Though mechanical exfoliation can offer graphene of higher quality but the efficiency goes low. It is difficult to regulate graphene quality, thus it needs an alternative approach for large-scale production. **Recent resolution of China of cutting down excavation of graphite on environmental grounds has imposed levy on battery or supercapacitor technology and hinders the required growth. Hence, a natural resource-based alternate is the need of the hour.**

1.3.1.2. Carbon nanotubes

Carbon nanotubes (CNTs) have been considered as an attractive electrode for supercapacitors due to its high strength, thermal stability, strong electrical conductivity, electrolyte accessibility and chemical stability. They are tubular-shaped materials and made up of graphene sheets that have been folded up to create hollow cylindrical nanostructures. CNTs are classified into two types based on number of graphene sheets present in the tubular morphology **(Zhang & Li, 2009):**

(i) Single-walled CNTs (SWCNTs) and

(ii) Multi-walled CNTs (MWCNTs).

The SWCNT is a single rolled graphene sheet. The tube diameter measures just only 1-2 nm. The MWCNT has many concentric graphene tubes coaxially arranged, upto a diameter of 100 nm **(Baughman et al., 2002).** In CNTs, the pores are in the mesoporous size, not in the micropores regime, as they are in activated carbons (ACs). As a result, the surface area of CNTs is less than the ACs. Also, CNTs suffer from high cost and harsh preparation condition for scalable production. Preparation of carbon nanotubes from several carbon resources say Molasses, glucose, fructose has all been tried. But either yield is low, or the large-scale production goes infeasible. Thus, scope of carbon nanotubes are limited.

1.3.1.3. Activated carbon

Activated carbon (AC) is one of the allotropes of carbon widely used due to the large surface area and porous structure. ACs have pores namely micropores (< 2 nm), mesopores (2-50 nm), and macropores (>50 nm) **(Abioye & Ani, 2015; Singh et al., 2016)**. It can be prepared by pyrolyzing the raw materials and then activating the carbonaceous precursors by either physical or chemical methods **(Heidarinejad et al., 2020)**. In physical method, high temperature activation is done under oxidizing atmosphere and in chemical method, activating agents are used in the raw materials at elevated temperature. Higher yields and well-developed pore architectures have been achieved by chemical activation process due to its simple and lower temperature process **(Bouchelta et al., 2008).**

Usually, activated carbon has been synthesized from coal or petrochemical products (non-biomass precursors). **In this scenario, it is critical to discover and use renewable resources for the preparation of activated carbon for supercapacitor applications in order to avoid high cost**. As a result, in recent years, several studies have been concentrated on the preparation of carbon materials from economically viable biomass towards energy storage devices in achieving high performance.

1.3.2 Transition Metal Oxides (TMOs)

Transition Metal Oxides (TMOs) have high relevance in the field of science and technology. An extensive choice and combinations of TMOs are available. The choice of metal compounds and complexes can be tuned depending on the target applications. They form variety of combinations but especially, stannates, nickelates, ferrites and cobaltites are very popular for different applications including supercapacitors.

Ruthenium oxide (RuO_2) is one of such promising candidate due to its high theoretical specific capacitance of ~1400–2000 Fg^{-1} **(Majumdar, 2018).** The electrochemical performance of RuO_2 is very popular for the rectangular shaped cyclic voltammogram.

Hydrous forms of RuO_2 have been studied intensively in supercapacitors because of the high theoretical specific capacitance of 1358 Fg^{-1} and electrical conductivity of 300 Scm^{-1} **(Lokhande et al., 2011).** Experimental specific capacitance up to 750 Fg^{-1} and 800-1200 Fg^{-1} have been reported for electrodeposited RuO_2 and hydrous RuO_2/carbon composites **(Jow & Zheng, 1995)** The major disadvantage of metal oxides is the low operating voltage. Materials like RuO_2 can only be applied with aqueous electrolytes which set the voltage around 1 V. Previously, RuO_2 electrode in H_2SO_4 electrolyte shows a maximum potential range of 1.4 V **(Lokhande et al., 2011)**. However, their performance has been limited to practical applications due to high cost and toxicity. Therefore, much effort has been made to search for inexpensive next-generation transition metal oxides with high performance.

1.3.2.1 Binary Transition metal oxides

In recent years, the harsh reality has generated a slew of social issues, prompting researchers to look for efficient ways to build high-performance supercapacitors **(Dong et al., 2012).** Because of the excellent electrochemical characteristics, cost effectiveness and environmentally benign, the researchers are focusing on binary transition metal oxides (BTMOs) as supercapacitor electrode materials. When compared to single metal oxides, binary metal oxides (BTMOs) provide rich redox reactions and combine the contributions of two different types of ionic species. For example, the electrochemical activity of $NiCo_2O_4$ could be improved by substituting Ni for Co in the spinel Co_3O_4 lattice **(Yu et al., 2014).** As a result, BTMOs have sparked a lot of interest in supercapacitor applications.

1.3.2.2. Spinel structure

Spinel structured metal oxides have given important roles in the applications of data storage, biotechnology **(Kim et al., 2005; Ounnunkad & Phanichphant, 2012; Vomir et al., 2016)** electronics **(Bitla et al., 2015)**, laser **(Molla et al., 2014)** and energy storage/conversion **(Shanmugavani & Selvan, 2016; Wei et al., 2016; Whittingham, 2004)** due to its several interesting properties including magnetism **(Marco et al., 2001)** optics **(Sonoyama et al., 2006)**, electricity **(Cho et al., 2011; Kushwaha et al., 2017; Naveen et al., 2015)** and catalysis **(Kaczmarczyk et al., 2016; Liang et al., 2011).**

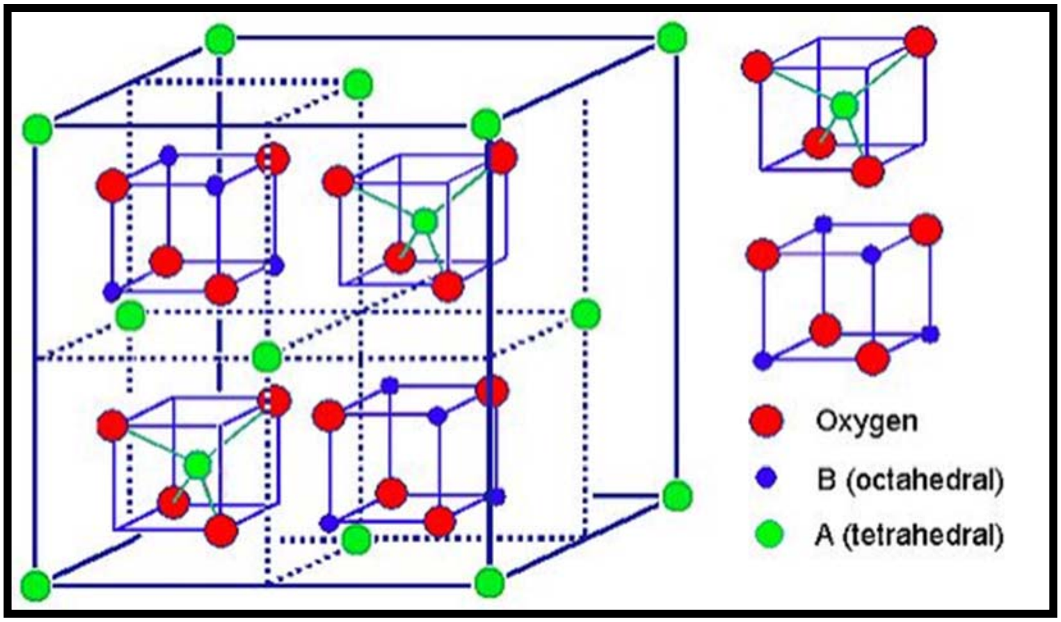

Figure 3 - Atomic arrangements of Spinel structured metal oxides

Spinel structure has the general formula of AB_2O_4, in which A and B are cations that are distributed in tetrahedral and octahedral positions in different ratios respectively. Figure 3 represents the spinel structured metal oxides and is obtained from **(Issa et al., 2013)**. They are divided into three types depending on their cation distribution in tetrahedral and octahedral sites:

- ✓ normal,
- ✓ inverse, and
- ✓ complex spinels **(Goodenough & Loeb, 1955, Grimes et al., 1989, Seko et al., 2006)**

A most accurate formula ($A_{1-\lambda}B_{\lambda}(A_{\lambda}B_{2-\lambda})X_4$) has been introduced in review article by **(Zhao et al., 2017)** to distinguish the spinels. For a normal spinel, $\lambda = 0$, then it has a formula of $A^{2+}(B^{3+}{}_2)O_4$. In which, the divalent cations (A) occupies the tetrahedral sites and the trivalent cations (B) occupies the octahedral sites (i.e., $[A]^{tet}\,[B_2]^{oct}O_4$). $ZnFe_2O_4$, $MgAl_2O_4$, $CoAl_2O_4$ are the examples of normal spinel. For inverse spinel, $\lambda = 1$ (Formula: $B(AB)O_4$). In this type of spinel, divalent cations occupies the octahedral sites and the trivalent cations are equally divided among the tetrahedral sites and remaining octahedral sites which can be represented by $[B]^{tet}[AB]^{oct}O_4$. $NiFe_2O_4$ is an example for an inverse spinel.

In complex spinel or random spinel, λ has the values between 0 and 1. i.e., the complex spinels lies between the normal and inverse spinels. E.g., $CuAl_2O_4$ in which both Cu^{2+} and Al^{3+} cations occupy the octahedral and tetrahedral sites by sharing.

1.3.2.3. Spinel structured Cobaltites:

Broad range of spinel structured metal oxides have been reported for energy storage devices. Among the various reported spinel structured metal oxides, cobaltites (MCo_2O_4; M=Zn, Ni, Cu, Mn etc) have been considered as an efficient electrode material for supercapacitor applications due to its high electrochemical stability, abundant resources and low cost **(Rajesh et al., 2016)**. For the betterment of the electrochemical performance of cobaltites, several efforts have been attempted such as different nano-structured morphologies, doping with suitable elements, preparing the composite material etc. Few reports are found with the dopants that are successful at enhancing the electrochemical activity.

In addition to electrodes, separators and electrolytes are other important contributors in a supercapacitor device.

1.4. Separators

Separators are thin membranes which are used to separate electrodes and let ions to pass through for intercalation with electrodes. Commonly, the separators are used when assembling the device with liquid electrolyte, hence, it prevents short circuit due to the direct electrical contact between two electrodes. Apart from polypropylene and polyethylene **(Szubzda et al., 2014)** separators, cellulose-based separators have been used in the supercapacitors due to its better wettability **(Perez-Madrigal et al., 2016)**. Separators have chosen to be very thin and flexible to enhance ionic transport and overall electrical conductivity of the cell. Separators are chosen with less weight so that they don't reduce the total energy density of the assembled device.

1.5. Electrolytes

Electrolytes are the medium for transferring the ions between the electrodes. To prevent short-circuiting, it should be ionically conducting and electrically insulating. Traditionally, majority of electrolytes are liquid. Electrolytes are categorised as aqueous or non-aqueous (organic) electrolytes **(Pal et al., 2019)**. The most common organic electrolytes for supercapacitor applications are such as *$TEABF_4$* (Tetraethylammonium tetrafluoroborate) *with PC (polyethylene carbonate)* and *$SBPBF_4$* (spiro-(1,1′)-bipyrrolidinium tetrafluoroborate) (**Jung et al., 2013; Lei et al., 2013; Perricone et al., 2013**) along with acetonitrile. The most used aqueous based electrolytes are KOH (Potassium hydroxide), Na_2SO_4 (sodium sulfate), H_2SO_4 (sulfuric acid**) (Han et al., 2014; Jiménez-Cordero et al., 2014; Pal et al., 2019)**

The choice of electrolyte material focuses on safety aspects and high-performance energy storage devices. SCs with aqueous electrolytes have high conductivity and capacitance, but it suffers from the low energy density, cycling stability and leakage problem. Organic electrolytes and ionic liquids (ILs) are operated at higher voltages, but it suffers from lower ionic conductivity. To overcome these challenges, supercapacitor devices with improved energy and power density and safety aspects are being researched. Based on several surveys, the challenges in supercapacitors can be solved using solid state electrolyte.

1.5.1 Solid state electrolytes

Solid state electrolytes have attracted the researchers due to the ever-increasing demand for power in portable and wearable electronic devices. They have lot of advantages over other electrolytes such as good ionic conducting media, simple packaging, liquid-leakage free, etc. Among various solid electrolytes, polymer-based electrolytes due to the demand for power and expectation of comfort in terms of probability and wearability of devices. It can be divided into three types such as Solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and polyelectrolytes. Among these, gel polymer electrolytes have the highest ionic conductivity and it possess tuneable morphology and bendable structures for various applications. Hence, they are dominating in SCs. A number of polymer hosts have been explored for preparing gel polymer electrolytes such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(ether ether ketone) (PEEK), poly(acrylic acid) (PAA), etc. From these polymers, poly(vinyl alcohol) is a widely explored polymer matrix due to its stability, low-cost, environmental friendliness. In PVA-KOH gel polymer electrolyte, the OH^- ions can easily move throughout the polymer matrix which enhance the performance of the supercapacitor device.

1.6. Need of the research work

The widespread use of supercapacitors has been limited to few applications due to the low energy density. The extensive research efforts are made to achieve the goal of high energy density without sacrificing their power density and cycling stability. With the rapid growth of supercapacitors, a single material is aimed to attain these two criteria. In this work, an attempt has been made to achieve commensurate energy and power density by assembling different devices out of improved and large scale feasible, cost-effective electrodes say, carbon from biomass of *P. juliflora* prepared with two different methods - Conventional heating and Plasma firing, $ZnCo_2O_4$ with sol-gel method. A systematic approach on symmetric and asymmetric supercapacitors with the improved electrodes are evaluated. A flexible supercapacitor is a demand of the day for wearable electronics, point of care devices and any other portable power demanding appliances and is addressed in this work.

1.6.1. Objectives of the research work

- To construct a supercapacitor for energy storage which is activating agent free and environmental friendly.
- To arrive at a flexible supercapacitor suitable for wearable electronics.

1.6.2. Methodology

- To prepare carbon from *Prosopis juliflora* biomass in ambient atmosphere through (i) low temperature conventional heating method, (ii) short impulse plasma method and analyse its electrochemical evaluation.
- To synthesize $ZnCo_2O_4$ metal oxide and evaluating its electrochemical performance.
- To fabricate symmetric supercapacitor device with the prepared electrode materials and study the electrochemical performance.
- To assemble asymmetric supercapacitor device with different combinations of prepared electrode materials and study the electrochemical performance of the devices.