2

Review of Literature

2.1. Introduction

In this Chapter, review of literature is devoted to the supercapacitor applications of carbon from various biomass and $ZnCo_2O_4$ electrode material. Especially, various nanostructures of $ZnCo_2O_4$ are detailed in this Chapter. Moreover, the performance of the symmetric and asymmetric device with activated carbon and Zinc cobaltite have been reviewed in this Chapter.

2.2. Review on Carbon

Carbonaceous materials with porous structure have been regarded as promising electrode materials for supercapacitors because of their outstanding characteristics such as tuneable morphology, stability, electrical conductivity, and functionality. In particular, activated carbons have been widely investigated and used in commercial EDLCs based on their relatively low cost, large specific surface area (generally > 1000 m^2g^{-1}), high electrical conductivity, environmental friendliness, chemical stability and availability, and easiness for scalability. Conventionally, porous carbon materials are prepared via harsh synthetic routes with high energy consumption using coal or petrochemical products as precursors. It is very important to develop and utilize renewable resources for the production of porous carbon materials for supercapacitor applications. In particular, the agricultural and forestry biomass materials are promising carbon precursor for preparing porous carbons due to its natural abundance, low-cost and environmental friendliness. Thus, the design of biomass-derived electrode materials has attracted extensive attention for the future development of supercapacitors. Few literatures based on biomass activated carbon for supercapacitor applications are described below.

A sustainable carbon has been synthesized by **Shen et al., (2019)** via thermal pyrolysis and with KOH activation from orange peel bio precursor. The activated carbon at 800°C relatively possess high BET surface area of 2004 m^2g^{-1} with multilevel of pores which provides plenty of space for the storage of electrolyte ions, contributing to good electrochemical performance i.e., specific capacitance of 306 Fg^{-1} at 0.5 Ag^{-1}.

Carbon from wild fungus sharia bambusicola has been prepared by **Hu et al., (2019)** The preparation procedure involves pre-carbonization, KOH activation and carbonization processes. Due to the hierarchical porous nature, effect of heteroatom doping, larger surface area (1556 m^2g^{-1}), the prepared material shows a higher specific capacitance of 339 F g^{-1} at 0.5 A g^{-1}. In addition, 98 % capacitance retention is obtained over 5000 cycles.

Chlorella biomass has been chosen by **Han et al., (2019)** as a precursor to synthesize the activated carbon using KOH activation followed by conventional heating method under N_2 atmosphere. After KOH activation, the surface of the chlorella derived carbon become more porous. The hierarchical pore structure provides a facile ion pathway, which could improve the specific capacitance of 142 Fg^{-1} at 1 mA/cm^2.

The performance of carbon materials prepared from corn stalk at different temperatures of 500 °C, 600 °C, 700 °C and 800 °C using conventional heating method under N_2 atmosphere have been investigated by **Yu et al., (2018)**. The highest specific surface area of 2349.89 m^2 g^{-1} has been achieved for prepared carbon sample at 700°C and exhibits the specific capacitance of 140 Fg^{-1} whereas in the case of carbon materials at 500 °C, 600 °C and 800 °C shows specific capacitance of 50, 64 and 105 Fg^{-1} respectively.

Porous activated carbon prepared from Couroupita guianansis (CG) flower has been prepared by **Elanthamilan et al., (2018)** and the TEM micrographs of carbon prepared at 800□C sample shows the interpenetrating macropore morphology. Such type of pores enhances the contact between the electrode–electrolyte interface and reduces the ion diffusion pathways and delivered only a minimum diffusive resistance. Hence, the electrochemical studies show an excellent specific capacitance value of 711 Fg^{-1} at 1 Ag^{-1}. It also exhibits the capacity retention of 92%, even after 5000 charge and discharge cycles.

Natural flax biomass precursor is used by **Jakubec et al., (2021)** to prepare the activated carbon by hydrothermal conversion and pyrolytic-chemical activation with potassium hydroxide. The as-prepared Activated carbon (AC) possess specific surface area of 1649 m^2g^{-1} accompanied by a microporous structure with the size of pores > 2 nm. These unique features of flax-derived ACs shows the specific capacitance of 500 Fg^{-1} at a current density of 0.25 A g^{-1} in standard three electrode configuration along with 85% retention after 150,000 charging/discharging cycles. The assembled symmetric supercapacitor with prepared AC and KOH electrolyte shows an energy density of 6.58 Wh Kg^{-1} and power density of 250 W Kg^{-1}.

A two step carbonization and KOH activation process have been reported by **Li et al., (2021a)** to prepare Co-doped (nitrogen and oxygen) porous carbon from yam waste biomass and the corresponding prepared AC shows a specific surface area of 2382 m^2g^{-1}. In the three electrode configuration, the specific capacitance of the prepared material is reached to 423.23 Fg^{-1} at 0.5 Ag^{-1} with a capacity retention of 96.4% at a high current density of 10 Ag^{-1} after 10,000 cycles in 6 M KOH electrolytic solution. Moreover, assembled symmetrical supercapacitor with the electrodes adopted the as prepared carbon in 6 M KOH electrolyte which demonstrates a specific capacitance of 387.3 Fg^{-1} at 0.5 Ag^{-1} with an energy density of 34.6 Wh Kg^{-1} at the power density of 200.1 W Kg^{-1}.

Waste coffee ground based activated carbon have been prepared by **Chiu & Lin, (2019)** through conventional carbonization followed by activation method. Different activation agents such as KOH, NaOH, HCl, H_3PO_4, $ZnCl_2$ and $FeCl_3$ have been used to prepare the activated carbon. Among these, carbon sample prepared by KOH activation exhibits specific capacitance of 105.3 Fg^{-1} due to large surface area (1250 m^2g^{-1}) in supercapacitor applications. An assembled symmetric supercapacitor with the as-prepared activated carbon shows an energy density of 6.94 Wh Kg^{-1} and 350 W Kg^{-1}.

Citric-acid-crosslinking and KOH-activating method have been reported by **Du et al., (2019) t**o synthesize the carbon from wheat straw. As prepared AC shows the hierarchical structure with mesopores. It exhibits a maximum specific surface area and specific capacitance of 2115 m^2g^{-1} and 294 Fg^{-1} when the ratio of KOH is 5 times than that of the biomass. Further, when assembled in symmetric device with PVA-KOH gel polymer electrolyte shows an energy density of 14 Wh kg^{-1} and power density of 440 W Kg^{-1}.

Sponge like porous carbon has been developed by **Liu et al., (2019)** using pomelo peel biomass precursor at 500°C, 600°C, 700°C and 800°C. It has been prepared by pre-carbonization followed by carbonization under N_2 atmosphere. At 600°C, it possess large surface area of 1193 m^2g^{-1} and the maximum specific capacitance of 310 Fg^{-1}.

After 10000 cycles, the capacity retention is 98.8 % at a current density of 2 Ag^{-1} in 6 M KOH electrolytic solution is obtained. In the symmetric supercapacitor device assembly, the prepared electrodes exhibit the maximum energy density of 21.4 Wh Kg^{-1} at a power density of 259.9 W Kg^{-1}.

Lotus leaves biomass derived carbon has been reported by **Lu et al., (2020)** using two-step activation method (HNO_3 -first-step activation and KOH – second step activation) along with hydrothermal method. The prepared carbon possess surface area of 2351 m^2g^{-1} and abundant micropores and mesopores structures. Hence, it exhibits capacitance of 478 Fg^{-1} in a three-electrode system at a current density of 1 Ag^{-1}. Besides, the assembled symmetric supercapacitor in a two-electrode system consists of prepared carbon delivers the specific capacitance of 358 Fg^{-1}, energy density of 14.2 Wh Kg^{-1} and power density of 285.6 W Kg^{-1}.

Hierarchical nano-structured activated carbon prepared from the banana peel biomass precursor has been examined by **Fasakin et al., (2018)**. In this work, biomass is pre-carbonized by hydrothermal method, activated by KOH agent and carbonized at different temperatures ranging from 750°C to 950 °C using conventional heat treatment method under Ar atmosphere. The prepared carbon sample obtained from the 900°C carbonization temperature (ABP900) exhibits unique material properties such as hierarchical porous nano-architecture containing micropores, and mesopores with the highest specific surface area 1362 m^2g^{-1}. Electrochemical performance has been analyzed for ABP900 at 1M $NaNO_3$ neutral aqueous electrolyte which shows the specific capacitance of 115 Fg^{-1} and the assembled symmetric device with 1M $NaNO_3$ operated in a potential window of 1.8 V, which exhibits a specific capacitance of 165 Fg^{-1} with an energy density of 18.6 Wh Kg^{-1} at 0.5 Ag^{-1}.

Activated carbon from the baobab fruit shells have been synthesized by **Mohammed et al., (2019)** using KOH and H_3PO_4 activation. The prepared material exhibits the high specific capacitances of 233.48 Fg^{-1} and 355.8 F g^{-1} at a current density of 1 Ag^{-1} with KOH and H_3PO_4 activation. Furthermore, the as-assembled flexible all-solid-state supercapacitor device based on the prepared material shows the higher specific capacitance of 58.67 Fg^{-1} at 1 Ag^{-1} and a high energy density of 20.86 Wh Kg^{-1} at a power density of 400 W Kg^{-1}.

N,S-doped activated carbon has achieved by hydrothermal reaction with KOH from elm (EL) flower biomass and reported by **Chen et al., (2018).** The EL-derived activated carbon (ELAC) shows Brunauer−Emmett−Teller (BET) surface area of 2048.6 m^2g^{-1} and specific capacitance of 275 Fg^{-1} at a current density of 1 Ag^{-1} and retained a capacitance of 216 Fg^{-1} at 20 Ag^{-1}. In addition, a symmetric supercapacitor assembled with N,S-self-doped activated carbon provides a capacitance of 62 Fg^{-1} at a current density of 10 Ag^{-1}, with energy and power densities of 16.8 Wh Kg^{-1} and 600 W Kg^{-1}.

Natural casings biomass has been used to prepare the N-enriched multi-layered porous carbon, reported by **Xu et al., (2018).** It exhibits surface area of 3100 m^2g^{-1} and high specific capacitance of 307.5 Fg^{-1} at a current density of 0.5 Ag^{-1} in 6 M KOH aqueous solution. It shows excellent cycling stability of 92.9 % capacitance loss 2 after 5000 cycles. Furthermore, the fabricated symmetrical supercapacitor with prepared carbon with a wide voltage window of 1.4 V delivers an energy density of 11.6 Wh Kg^{-1} at a power density of 297 W Kg^{-1}.

Table 2 – Report on carbon prepared from various biomass and its comparative electrochemical performance

S.No	Reported by	Biomass and method of preparation	Performance of electrode in three electrode configuration		Performance of supercapacitor assembly	
			Electrolyte	Performance	Configuration	Performance
1.	**Li et al., (2021)**	Tobacco biomass Pre-carbonization, activation and carbonization under N_2 atm.	KOH	C_s- 324 Fg^{-1}	-	
2.	**Lu et al., (2020)**	Pitaya peel Pre-carbonization activation and carbonization under N_2 atm	KOH	C_s- 255 Fg^{-1}	-	-
3.	**Lan et al., (2020)**	Walnut shell and activation and pyrolysis under N_2 atm.	KOH	C_s-169 Fg^{-1}	-	
4.	**Awasthi et al., (2019)**	*Wisteria sinensis* Pre-carbonization, activation and carbonization under N_2 atm.	H_2SO_4	C_s- 110 Fg^{-1}	-	-
5.	**Sodtipinta et al., (2017)**	Pineapple leaves Pre-carbonization, activation and carbonization under Ar atm	Na_2SO_4	C_s- 131.3 Fg^{-1}	-	-
6.	**Wang et al., (2016)**	Cabbage leaves Pre-carbonization activation and carbonization under Vacuum	KOH	C_s -336 Fg^{-1}	-	-
7.	**Jain et al., (2021)**	European deciduous trees Pyrolysis and cavitation	H_2SO_4	C_s- 75 Fg^{-1}	Symmetric device: Anode: Activated carbon Electrolyte: H_2SO_4	Energy density 0.53 Wh Kg^{-1} Power density 51 W Kg^{-1}

S.No	Reported by	Biomass and method of preparation	Performance of electrode in three electrode configuration		Performance of supercapacitor assembly	
			Electrolyte	Performance	Configuration	Performance
8.	**Selvaraj et al., (2020)**	Wood of *P.juliflora* Pre-carbonization, activation and carbonization under N_2 atm.	KOH	Cs- 588 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte: KOH	Energy density 56.7 Wh Kg^{-1} Power density 248.8 W Kg^{-1}
9.	**Mehare et al., (2020)**	Onion peel Pre-carbonization and Pyrolysis	H_2SO_4	C_s -127 Fg^{-1}	Symmetric device: Anode: Activated carbon Electrolyte: H_2SO_4	Energy density 13.61 Wh Kg^{-1} Power density 200.8 W Kg^{-1}
10.	**Ahirrao et al., (2019)**	Sweet lime peel biomass, Activation and carbonization	H_2SO_4	C_s- 421 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte: $EMIMBF_4$	Energy density 45 Wh Kg^{-1} Power density 1600 W Kg^{-1}
11.	**Shanmugapriya et al., (2019)**	Pods of *P.juliflora* Pre-carbonization, activation and carbonization under Ar atm	H_2SO_4	C_s- 274 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte: 0.5M H_2SO_4 + 0.05M KI	Energy density 35.7 Wh Kg^{-1} Power density 971 W Kg^{-1}
12.	**Zhu et al., (2018)**	*Chlorella zofingiensis* Pre-carbonization, activation and heat treatment under Ar atm.	KOH	C_s- 353 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte: KOH	Energy density 20 Wh Kg^{-1} Power density 332 W Kg^{-1}
13.	**Han et al., (2018)**	Pueraria Pre-carbonization, activation and carbonization under N_2 atm	KOH	C_s- 250 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte:KOH	Energy density 8.46 Wh Kg^{-1} Power density 123 W Kg^{-1}
14.	**Wang et al., (2018)**	Sunflower stalk Pre-carbonization, activation and carbonization under N_2 atm.	KOH	C_s- 365 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte:KOH	Energy density 35.7 Wh Kg^{-1} Power density 989 W Kg^{-1}

S.No	Reported by	Biomass and method of preparation	Performance of electrode in three electrode configuration		Performance of supercapacitor assembly	
			Electrolyte	Performance	Configuration	Performance
15.	**Zhang et al., (2019)**	*Xanthoceras sorbifolia* Pre-carbonization, activation and carbonization under N_2 atm	KOH	C_s- 421 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte:KOH	Specific capacitance C_s- 276 Fg^{-1}
16.	**Tian et al., (2018)**	Rice stream Pre-carbonization, activation and carbonization under N_2 atm	KOH	C_s-377 Fg^{-1}	Symmetric device: Anode: Activated carbon Electrolyte: KOH	Energy density 13 Wh Kg^{-1} Power density 250 W Kg^{-1}
17.	**Ochai-Ejeh et al., (2017)**	Quercus suber Activation and carbonization	1M Na_2SO_4	C_s- 166 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte: Na_2SO_4	Energy density 18.6 Wh Kg^{-1} Power density 449.4 W Kg^{-1}
18.	**Liu et al., (2017)**	Perilla Pyrolysis under N_2 atm	Na_2SO_4	C_s -270 Fg^{-1}	Symmetric device: Electrodes: Activated carbon Electrolyte: Na_2SO_4	Gravimetric energy density 14.8 WhL^{-1} and gravimetric power density 490 W L^{-1}
19.	**Su et al., (2017)**	Poplar catkins Carbonization and activation under N_2 atm	KOH	C_s- 314.6 Fg^{-1}	Symmetric device: Electrode: Activated carbon Electrolyte: Na_2SO_4	Energy density 20.86 Wh Kg^{-1} Power density 180.16 W Kg^{-1}
20.	**Wang et al., (2017)**	Willow catkins Pre-carbonization activation and carbonization under N_2 atm	KOH	C_s- 333 Fg^{-1}	Symmetric device: Electrode: Activated carbon Electrolyte: KOH	Energy density 8.8. Wh Kg^{-1} Power density 50 W Kg^{-1}

Based on the vast literature survey, carbon prepared from the bio based resources are highly preferable for supercapacitor electrode applications. Further, these carbons are highly porous, geometrically well arranged and cost effective sources. However preparation of carbons involes various processes such as physical activation process, physio-chemical activation process, conventional and chemical activation process. This mode of activation tend to cause environmental safety issues, kinetics dependence and temperature problems, difficulty in removal of chemical agent and consequent pore clogging and demands high cost of heating in large scale production of activated carbon (AC). But, in this work, an interesting and economic choice, is *Prosopis juliflora*, an unwanted widely invanted weed in the landscape of Coimbatore district, Tamilnadu, India is identified as a biomass precursor. The bark and stick of the *Prosopis juliflora* plant is taken for carbon preparation by conventional heating and plasma firing methods without any post activation. The findings and other discussions on this carbon material are provided in the forth coming Chapters.

2.3. Review on Zinc cobaltite

Spinel structured Co-based materials have received much attention because of its high theoretical specific capacitance, abundant supplement, environmental friendliness, and rich redox chemistry. Spinel materials, which have a typical chemical formula of AB_2O_4, have been widely recognised and concerned in the energy storage fields, including SCs, anode materials of lithium-ion batteries (LIBs), Li-ion capacitors, and Na-ion capacitors etc. When compared to monometallic oxides of A and B, spinel structured metal oxides show better electrochemical activity, electrical conductivity, and more numerous redox processes. However, the cyclic performance of transition metal oxides is inferior to that of pure EDLCs. MCo_2O_4 with varied nanostructures and proper crystal structure tailoring by element doping and oxygen vacancies outperforms the pristine MCo_2O_4 in terms of energy storage and structural stabilities. Among the various MCo_2O_4, $ZnCo_2O_4$ has been examined as a supercapacitor material because of their high specific surface area, consistent pore size distribution, higher reversible capabilities, good cycle stability, and ecologically benign nature.

Dual morphology of $ZnCo_2O_4$ has been developed by **Koyyada et al., (2021).** In this work, the two different $ZnCo_2O_4$ samples i.e., ZCO-15/Ni (nanoflowers) and ZCO-30/Ni (nanowires) which are achieved by adjusting its reaction time. The dual morphologies (nanoflowers and nanopetals) of ZCO-15/Ni are responsible for its structural stability and high electroactive surface area (25.61 m^2g^{-1}). Adhesion of particles on the Ni foam current collector enables the ion-electron transport easier in ZCO-15/Ni foam. Hence, the electrode delivers an excellent specific capacity of 650.27 Cg^{-1} at 0.5 Ag^{-1} and cyclic performance of 91% capacitance retention after 5000 cycles compared to ZCO-30/Ni electrode (311.10 Cg^{-1} and 89% of capacity retention).

Preparation of Zinc cobaltite ($ZnCo_2O_4$) nanostructures have been reported by **Silambarasan et al., (2021).** The FTIR and Raman spectrum confirmed the presence of surface functional groups and confirmed the formation of high-quality $ZnCo_2O_4$ nanocrystals. The FE-SEM and TEM analysis exhibits the bundle like morphology of the final product. Finally, the as-prepared $ZnCo_2O_4$ nanostructure demonstrates the specific capacitance of 159 Fg^{-1} at 2 mA cm^{-2} in 2 M KOH electrolyte and the long cyclic test showed the 92% initial capacitance retention over 2500 cycles.

Nanostructured $ZnCo_2O_4$ microstrips coated on a carbon cloth has been developed by **Patil et al., (2020)** using hydrothermal method for the supercapacitor application. The FE-SEM micrograph illustrates that the $ZnCo_2O_4$ material is composed of microstrips with ~0.5 µm width and length in micron uniformly covered the carbon cloth surface. The electrochemical analysis of $ZnCo_2O_4$ microstrips electrode achieves the highest specific capacitance of 1084 Fg^{-1} at 2 mV/s scan rate. Furthermore, the 96.2 % capacitive retention is obtained at a higher scan rate of 100 mV/s after 1000 CV cycles, indicating excellent cycling stability of the $ZnCo_2O_4$ microstrips electrode.

Microporous/nanoporous $ZnCo_2O_4$ (ZCOSNS) has been prepared by **Mohamed et al., (2019)** using H_2O_2-urea-supported hydrothermal reaction. The XRD and XPS results shows the prepared material have a spinel structure with high crystallinity and purity. Nanospherical morphology of ZCOSNS is seen in FESEM and TEM micrographs with a diameter of about 175-180 nm. It exhibits specific surface area of 21.13 m^2g^{-1}, high specific capacitance of 1596 Fg^{-1} at 1 Ag^{-1} and an excellent cycling stability (119% from initial value) even after 2000 cycles.

Porous $ZnCo_2O_4$ hierarchical microspheres have been prepared by **Chen et al., (2019)** using solvothermal method at 120 °C for 3h. The prepared $ZnCo_2O_4$ microspheres exhibits a specific surface area of 67.1 m2 g^{-1}. Accessibility of more number of ions/electrons in the obtained porous structure of $ZnCo_2O_4$ microspheres exhibits pseudocapacitive behaviour and it delivers a specific capacitance of 689 Fg^{-1} at 1 Ag^{-1}.

Hydrothermally synthesized $ZnCo_2O_4$ nanosheets have been reported by **Xiao et al.,** (**2018**). The obtained mesoporous $ZnCo_2O_4$ nanosheets exhibit a high specific surface area of 191.64 m^2g^{-1}. The prepared mesoporous $ZnCo_2O_4$ shows the high specific capacitance of 835.26 Fg^{-1} at the current density of 1.0 Ag^{-1} with 73.28% of capacity retention after 1000 continuous charge-discharge cycles at the current density of 8 Ag^{-1}.

Electrochemical performance of $ZnCo_2O_4$ have been improved by **Moon et al., (2018).** In this work, nitrogen is doped into pristine material using controllable NH_3 plasma treatment. It effectively changes the electronic and chemical properties of the pristine $ZnCo_2O_4$ by the nitrogen doping. The nitrogen (N)-doped $ZnCo_2O_4$ electrodes not only significantly enhances the electrical conductivity. Compared to pristine $ZnCo_2O_4$ (1682.2 Fg^{-1} at 5 Ag^{-1}), the N-doped $ZnCo_2O_4$ electrode without conductive additives possessed high specific capacitance of 3804.6 Fg^{-1} at 5 Ag^{-1} and good cycling stability (only 3.3% loss after 3000 cycles at 30 Ag^{-1}).

Hierarchical coral-like $ZnCo_2O_4$ nanowires have been analysed by **Rajesh et al., (2017)** for supercapacitor applications. It is achieved by a surfactant-free hydrothermal method. Unique coral-like $ZnCo_2O_4$ nanowires exhibits electroactive surface area of 29.36 m^2g^{-1}. Subsequently, the coral-like $ZnCo_2O_4$ nanowires exhibits specific capacitance of 694 Fg^{-1} at a current density of 2 Ag^{-1} and cycling stability of ∼85% after 2000 cycles at a charge-discharge current density of 10 Ag^{-1}.

Nanoflakes morphology of $ZnCo_2O_4$ has been developed by (Heydari & Gholivand, 2017) **Heydari et al., (2017)** using electrodeposition method. In this reported work, the $ZnCo_2O_4$ nanoflakes are grown on Ni foam and it exhibits electroactive surface area of 138.8 m^2g^{-1}. The porous structure improves the ion transfer pathways which can facilitate the electrochemical process. Hence, the specific capacitance of $ZnCo_2O_4$ nanoflakes is 1781.7 Fg^{-1} at a current density of 5 Ag^{-1} along with 92% of the initial capacitance maintained after 4000 cycles.

$ZnCo_2O_4$ nanoparticles (NPs) with four different mass ratios of polyvinyl pyrrolidone (PVP) with respect to metal oxides have been reported by **Tomboc et al., (2016) .** In this work, the four different samples are, 0.55 wt% PVP (P1), 1.09 wt% PVP (P2), 1.64 wt% PVP (P3) and 2.18 wt% PVP (P4), prepared by hydrothermal method. The prepared sample exhibits four different morphology with four different PVP ratio i.e., rods, ring, oval “rice grain” and hexagonal-like shaped $ZnCo_2O_4$ NPs. The ring-like morphology (P2) can be accounted to its hierarchical structure consisting of a huge number of spherical nanoparticles, which may have provided a special structure with easier path for the transfer of electrons, thus improving the specific capacitance which shows the highest specific capacitance of 2834.18 Fg^{-1} at a scan rate of 2 mVs^{-1} and excellent cycling ability after 3000 cycles at 50 mVs^{-1} scan rate.

Flower like $ZnCo_2O_4$ microspheres grown on Ni foam have been investigated by **Fu et al., (2015)** using hydrothermal method. Electrochemical performance confirms that the $ZnCo_2O_4$ microspheres exhibits pseudocapacitive behaviour along with the specific capacitance of 687.1 Fg^{-1} at 1 Ag^{-1} and excellent cycling stability of 97.1% after 1500 cycles.

Reflux condensation method has been adopted to prepare the $ZnCo_2O_4$ nanostructures and reported by **Kamble et al., (2021).** The prepared Zinc cobaltite is grown on flexible stainless-steel mesh (FSSM) substrate at different temperatures. The $ZnCo_2O_4$ nanorods synthesized at 120°C shows a higher specific capacitance of 315 Fg^{-1} at 2 mA cm^{-2} with 6 M KOH electrolytic solution. The fabricated asymmetric device with the configuration of $ZnCo_2O_4$ nanorod (anode)/ PVA-KOH /$FeCo_2O_4$ nanosheet (cathode) is operated at a potential of 1.4 V that demonstrated a specific capacitance of 108.4 Fg^{-1} at 6 mA cm^{-2} and an energy density of 25.45 Wh Kg^{-1} (power density of 3620 WKg^{-1}) with cyclic stability of 77% capacitance retention over 3000 cycles.

$ZnCo_2O_4$ quasi-cubes have been developed by **Chen et al., (2020)** using solvothermal method with help of glycerine. The shape of the Zinc cobaltite depends on the volume ratio of water to glycerine. $ZnCo_2O_4$ microspheres have been attained when the volume ratio of water to glycerine is set to be 1/3 and $ZnCo_2O_4$ quasi-cubes formed when the ratio of water is equal to glycerine. These QCs exhibits the large surface area of 83.9 m^2g^{-1} along with pore size distribution at 2.1 nm. Due to the mesoporous structure of

$ZnCo_2O_4$, QCs more active sites involved in the electrochemical reactions. Hence, $ZnCo_2O_4$ QCs achieves a high specific capacitance 804 Fg^{-1} at 1 Ag^{-1} and 79.2% of capacitance retention after 3000 cycles. Moreover, $ZnCo_2O_4$ QCs//AC ASC has been fabricated and it exhibits an energy density of 34.4 Wh Kg^{-1} at a power density of 860.1 W Kg^{-1}.

$ZnCo_2O_4$ ultra-thin curved sheets have been demonstrated by **Zhou et al., (2019)** using hydrothermal method and sodium dodecyl sulphate (SDS) surfactant. Addition of SDS enhances the utilization ratio of the active materials and contact between active material and current collector. Hence, $ZnCo_2O_4$ ultra-thin curved sheets exhibit the higher specific capacity of 832 Cg^{-1} at 5 Ag^{-1} and maintains cycling stability of 85.5% at 50 Ag^{-1} after 5000 cycles. Further, the fabricated button hybrid supercapacitor device (activated carbon and $ZnCo_2O_4$ ultra-thin curved sheets as anode and cathode) shows an energy density of 20.31 Wh kg^{-1} at a power density of 855 W kg^{-1} and cycling stability of 87% retention after 5000 cycles.

Porous network of $ZnCo_2O_4$ nanosheets have been tailored by **Li et al., (2019)** using hydrothermal technique at different annealing temperatures. At 200°C, it exhibits an ultrahigh areal capacitance of 3.19 Fcm^{-2} at a current density of 2 mA cm^{-2} due to the formation of smaller nanoparticles and pores which is convenience for transportation of electrolyte ions. The fabricated asymmetric supercapacitor device by $ZnCo_2O_4$ annealed at 200ºC and activated carbon as the positive and negative electrode, which shows the energy densities of 50.7 and 37.7 Wh Kg^{-1} at power densities of 187.6 and 2950.4 W Kg^{-1}.

Hexagonal prismatic nanocrystalline $ZnCo_2O_4$ (HPNZCO) has been reported by **Varalakshmi et al., (2019).** It is prepared by sodium dodecyl sulphate (SDS) assisted facile hydrothermal method at 150°C for 12 h. FESEM analysis shows homogenously distributed hexagonal prism grains with an average grain size of less than 10 nm. SDS surfactant is able to modify the surface chemistry of $ZnCo_2O_4$ by changing their hydrophobic or hydrophilic properties, hence it improves the contact between electrode and current collector which resulting in high specific capacitance of 1060 Fg^{-1} at a current density of 1 Ag^{-1} and 93% of capacitance retention even after 5000 cycles.

Hollow $ZnCo_2O_4$ microspheres have been prepared and also an asymmetric supercapacitor device has been fabricated by **Shang et al., (2018).** The hollow $ZnCo_2O_4$ microspheres synthesized by solvothermal and coordinating etching route have an uniform morphology and a specific surface area of 24.7 m^2g^{-1}. The $ZnCo_2O_4$ shows the high specific capacitance of 78.89 $mAhg^{-1}$ at current density of 1 Ag^{-1}. An asymmetric device fabricated by $ZnCo_2O_4$, KOH and activated carbon acts as cathode, electrolyte and anode. The fabricated device

Porous $ZnCo_2O_4$ nanostructures have been synthesized by **Xu et al., (2017)** using hydrothermal method. Due to the superiority of the porous nanostructure, the obtained $ZnCo_2O_4$ exhibit pseudocapacitive performance with specific capacitance of 776.2 F g^{-1} at 1 Ag^{-1} and good cycle stability (84.3% capacity retention at 3 Ag^{-1}). Further, a asymmetric supercapacitor device has been fabricated using the $ZnCo_2O_4$ as the anode assembled with the freeze-dried reduced graphene oxide (F-RGO) cathode which displayed an energy density of 84.48 Wh Kg^{-1} at the power density of 0.4 KW Kg^{-1}.

$ZnCo_2O_4$ nanoflakes have been prepared by **Kumbhar & Kim, (2018)**. In this reported work, Zinc cobaltite nanoflakes are prepared by electrodeposition and followed by the hydrothermal growth of MnO_2 nanosheets. The prepared $ZnCo_2O_4$ - MnO_2 heterostructured electrode exhibits a maximum specific capacitance of 2057 Fg^{-1} at a current density of 1 Ag^{-1} with a cycling stability of 96.5% after 5000 cycles. The assembled asymmetric device with activated carbon (AC) as the anode and $ZnCo_2O_4$ - MnO_2 as the cathode shows excellent pseudocapacitive performance with an energy density of 69 Wh kg^{-1} and maximum power density of 4.9 kW kg^{-1}.

Mesoporous $ZnCo_2O_4$ thin sheets (CQU-Chen-Zn-Co-O-1) have been prepared by **Song et al., (2017)** using hydrothermal method. It shows an areal capacitance of 2.72 Fcm^{-2} (2690.86 Fg^{-1}) at 2.02 $mAcm^{-2}$ and rate capability of 59.76 % from 1.01 to 10.1 $mAcm^{-2}$ along with cycling performance of 96.5% loss after 5,000 cycles. Further, the asymmetric supercapacitor device has been assembled by CQU-Chen-Zn-Co-O-1 as a cathode and activated carbon (AC) as an anode with KOH electrolyte. It exhibits high energy density of 33.98 and 9.78 Wh Kg^{-1} at power density of 8 and 0.8 KW Kg^{-1} with good cycling performance of 6.7 % loss after 10,000 cycles.

Micro-flowers and micro-sheets morphologies of $ZnCo_2O_4$ have been achieved by **Pan et al., (2017)** using hydrothermal method. The $ZnCo_2O_4$ micro-flowers offers specific capacitance of 2256 Fg^{-1} at 2 mA cm^{-2}, excellent rate capability of 84% when the current density is 20 mA cm^{-2} which is higher than $ZnCo_2O_4$ micro-sheets (specific capacitance of 2037 Fg^{-1} at 2 mA cm^{-2}). Such a high performance of $ZnCo_2O_4$ micro-flowers can be attributed to the structural factor, higher specific surface area and more convenient transport of electrons and electrolyte ions than $ZnCo_2O_4$ micro-sheets. The assembled supercapacitor configuration of $ZnCo_2O_4$ micro-flowers (cathode)/KOH (electrolyte)/ carbonized filter paper (anode) device shows an energy density of 46.3 Wh Kg^{-1} (power density is 634 W Kg^{-1}) at a current density of mA cm^{-2}.

3D hierarchical peony-like $ZnCo_2O_4$ have been proposed by **Shang et al., (2017)**. BET surface area analysis shows the pores and crevices which enhance ion transportation and provide numerous active sites for redox reactions. Hence, electrochemical tests reveal that the obtained $ZnCo_2O_4$ delivers a high specific capacitance of 440 Fg^{-1} at a current density of 1 Ag^{-1}, and has excellent cycling stability even after 3000 cycles. The asymmetric device is also fabricated with configuration of $ZnCo_2O_4$/KOH/AC which exhibits the maximum specific capacitance of 83.7 Fg^{-1} at the current density of 0.5 Ag^{-1}. Moreover, it shows a maximum energy density of 29.76 Wh Kg^{-1} at a power density of 398.53 W Kg^{-1}.

In such a way, the thrust for Zinc cobaltite and developing matching counterparts for supercapacitor applications is getting elevated every year. Few notable and successful Zinc cobaltite electrode material along with the assemblies of supercapacitor in recent years has been consolidated and reported in Table 3.

Table 3 – Reports on Zinc Cobaltite and its comparative electrochemical performances

S.No	Reported by	Material and method of preparation	Performance of three electrode configuration		Performance of supercapacitor assembly	
			Electrolyte	Performance	Configuration	Performance
1.	**Abdali et al., (2021)**	Zinc cobaltite-reduced graphene oxide $ZnCo_2O_4$-rGO and hydrothermal method	KOH	C_s -1242 Fg^{-1}	-	-
2.	**Samiei et al., (2021)**	$ZnCo_2O_4$ and hydrothermal method	KOH	C_s- 575 Fg^{-1}	-	-
3.	**Reddy et al., (2020)**	$ZnCo_2O_4$ and hydrothermal method	KOH	C_s- 421 Fg^{-1}	-	-
4.	**Yang et al., (2020)**	S-doped $ZnCo_2O_4$ microspindles and hydrothermal method	KOH	C_s- 522 Fg^{-1}	-	-
5.	**Han et al., (2019)**	$ZnCo_2O_4$ mesoporous microspheres	KOH	C_s- 588 Fg^{-1}	-	
6.	**Saravanakumar et al., (2019)**	$ZnCo_2O_4$ and hydrothermal method	KOH	C_s- 500 Fg^{-1}	-	-
7.	**Priya et al., (2019)**	$ZnCo_2O_4$ and hydrothermal method	KOH	C_s- 434 Fg^{-1}	-	-
8.	**Merabet et al., (2018)**	$ZnCo_2O_4$ and sol-gel method	KOH	C_s- 158 Fg^{-1}	-	
9.	**Yin et al., (2018)**	$ZnCo_2O_4$ nanosheet arrays and hydrothermal method	KOH	C_s- 1004.9 Fg^{-1}	-	-

S.No	Reported by	Material and method of preparation	Performance of three electrode configuration		Performance of supercapacitor assembly	
			Electrolyte	Performance	Configuration	Performance
10.	**Meng et al., (2020)**	$ZnCo_2O_4$@$CoMoO_4$ core-shell nanosheet arrays and hydrothermal method	KOH	C_s -1096.08 Cg^{-1}	Asymmetric device: Anode: Activated carbon Cathode:$ZnCo_2O_4$@$CoMoO_4$ Electrolyte: KOH	Energy density 29.24 Wh Kg^{-1} Power density 884.57 W Kg^{-1}
11.	**Cheng et al., (2019)**	$ZnCo_2O_4$ and hydrothermal method	KOH	C_s-1700 Fg^{-1}	Asymmetric device: Anode: Activated carbon Cathode:$ZnCo_2O_4$ Electrolyte:KOH	Energy density 63 Wh Kg^{-1} Power density 795.5 W Kg^{-1}
12.	**Bhagwan et al., (2019)**	$ZnCo_2O_4$/MWCNT and co-precipitation method	KOH	C_s- 64 mAh g^{-1}	Asymmetric device: Anode: Activated carbon Cathode:$ZnCo_2O_4$ Electrolyte:KOH	Specific capacitance 17 mAh g^{-1}
13.	**Mary & Bose, (2018)**	$ZnCo_2O_4$ and hydrothermal method	KOH	C_s- 290 Fg^{-1}	Symmetric device: Electrodes: $ZnCo_2O_4$ Electrolyte: KOH	Energy density 0.469 Wh Kg^{-1} Power density 22 W Kg^{-1}
14.	**Mary & Bose, (2017)**	Mn doped $ZnCo_2O_4$	KOH	C_s- 707 Fg^{-1}	Symmetric device: Electrodes: Mn doped $ZnCo_2O_4$ Electrolyte: KOH	Energy density 228 m Wh Kg^{-1} Power density 14.9 W Kg^{-1}

S.No	Reported by	Material and method of preparation	Performance of three electrode configuration		Performance of supercapacitor assembly	
			Electrolyte	Performance	Configuration	Performance
15.	**Gai et al., (2017)**	$ZnCo_2O_4$ microspheres and solvothermal method	KOH	C_s- 542.5 Fg^{-1}	Asymmetric device: Anode: Activated carbon Cathode: $ZnCo_2O_4$ Electrolyte:PVA-KOH	Energy density 21.97 Wh Kg^{-1} Power density 38.89 W Kg^{-1}
16.	**S. Sahoo & Shim, (2017)**	Zinc cobaltite/nitrogen-doped reduced graphene oxide (ZNGN) composite and hydrothermal method	KOH	C_s-1613 Fg^{-1}	Asymmetric device: Anode: rGO Cathode:ZNGN Electrolyte:PVA-KOH	Energy density 36.5 Wh Kg^{-1} Power density 1402 W Kg^{-1}
17.	**Omar et al., (2017)**	PANI-$ZnCo_2O_4$ nanocomposite and hydrothermal method	KOH	C_s -398 Cg^{-1}	Asymmetric device: Anode: Activated carbon Cathode: PANI-$ZnCo_2O_4$ nanocomposite Electrolyte: KOH	Energy density 13.25 Wh Kg^{-1} Power density 375 W Kg^{-1}
18.	**Raut & Sankapal, (2017)**	Zinc cobaltite ($ZnCo_2O_4$) film by successive ionic layer adsorption	KOH	C_s- 675 Fg^{-1}	Symmetric device: Electrodes: $ZnCo_2O_4$ Electrolyte: KOH	Energy density 9.61 Wh Kg^{-1} Power density 1450 W Kg^{-1}

Most of the reported literatures reported the hydrothermal method to prepare Zinc cobaltite. The structure reproducibility of the material prepared from the hydrothermal method depends on different factors such as kinetics, duration of heating, pressure and temperature of synthesis which are to be critically controlled and not favourable for large scale production. Hence, high challenge is faced towards restoring structural reproducibility in large scale. It is obvious that the production cost even if the structural reproducibility is achieved would be high thus preventing such method from commercialization. So, in this present work, Zinc cobaltite has been prepared by facile sol-gel method to improve the structural reproducibility.

2.4. Summary

Based on the literature, it is clear that, almost all the reports on carbon derived from the biomass involves post activation method during synthesis process. Hence, the removal of chemicals from the material leads to increase in cost of the preparation method for large scale production and leads to environmental issues of handling the sumptuous quantities of acids and acidic water used for removal. This has been solved by attempting the preparation of carbon from biomass precursor without any post activation. Also, Spinel structured metal oxides have been chosen as an electrode due its earth abundance. Its performance strongly depends on the morphology of the material. Hence, the researchers have been made various efforts to achieve different morphology using different preparation methods. Based on the literature, the widely used synthesis method for Zinc cobaltite, is, hydrothermal method. However, hydrothermal method is not feasible for large scale production due to it’s the high kinetic dependency. Hence, in the present work, Zinc cobaltite has been prepared by simple sol-gel method. Also, employed the prepared anode (carbon based material) and cathode (Zinc cobaltite based materials) as an electrode material for assembling symmetric and asymmetric supercapacitor.