2 REVIEW OF LITERATURE

The electrochemical properties of energy storage devices, such as lithium-ion batteries (LIBs) and supercapacitors, can be distinguished based on factors like electrode material, electrolyte, and cell design. Electrode materials play a crucial role in determining the electrochemical performance of the cell, with surface characteristics being a significant factor. There are six primary categories of electrode materials, namely carbon-based materials, transition metal oxides, conductive polymers, metal oxides-carbon composites, conductive polymers-carbon composites, and hybrid metal oxide-conductive polymer materials **(Liu *et al.*, 2019, Şahin *et al.*, 2022)**

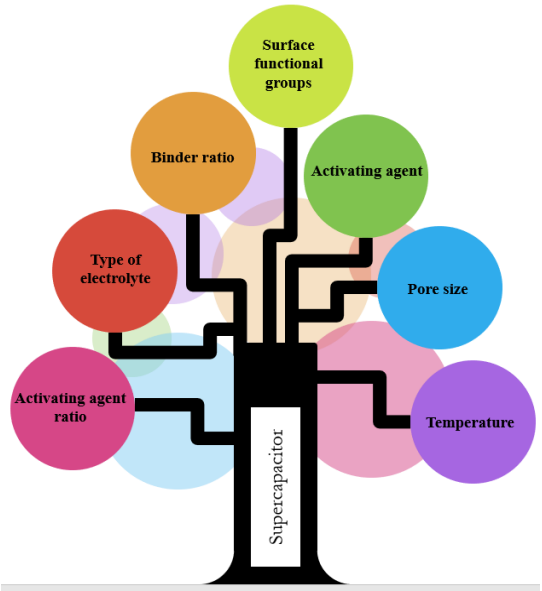

Figure 2.1: Factors that influence capacitance of supercapacitors.

This chapter provides a comprehensive review of the literature on biomass carbon electrode material and its factors that affecting the capacitance utilized in LIBs and supercapacitors, exploring each in detail in the subsequent sections.

2.1. Prospects of carbon-based electrode materials in Supercapacitors

Carbon-based materials, including Activated Carbons (ACs), carbon aerogels, graphite, carbon nanotubes, carbon nanofibers, and nano-sized carbon, have been actively studied as potential electrode materials for energy storage devices. This interest stems from their accessibility, ease of processability, non-toxic nature, high chemical stability, and a wide working temperature range. Currently, Activated Carbons (ACs) are extensively employed due to their notable porosity and high surface area.

Ongoing research focuses on enhancing energy storage capacity in devices like LIBs and capacitors, with a concurrent emphasis on reducing CO_2 emissions. The structural or

physical attributes of carbon materials used as electrodes, or chemically modified carbon surfaces, are promising avenues for improvement. Notably, carbon demonstrates significant potential across various applications and devices, with several carbon varieties obtained through the pyrolysis of biomass precursors. Utilizing biomass waste for carbon production is economically advantageous, making it a viable raw material for generating porous carbons that exhibit favourable electrochemical capacitive performance in capacitors and cycling efficiency in lithium-ion cells.

Biomass materials, particularly the end products of pyrolysis or thermal processing, such as biomass carbon or biochar, exhibit suitability for energy and power devices, primarily as electrodes. Various research groups have extensively investigated the effective utilization of biomass-derived carbons as electrode materials in electrochemical energy systems like LIBs and supercapacitors. The subsequent sections of this review provide comprehensive insights into the electrochemical performance of carbon materials derived from biomass.

2.2. Utilization of biomass carbon as an electrode material in supercapacitors

Biomass serves as a substantial source for carbon-based electrode materials in supercapacitors. The primary biomass sources encompass

- Agricultural/ Plant wastes
- Industrial wastes
- Domestic wastes
- Marine wastes

This section provides detailed insights into the preparation methodologies, physical characteristics, and electrochemical properties associated with biomass-derived carbon, categorized under the mentioned titles.

2.2.1. Biomass carbon from agricultural waste

Tadesse *et al.*, (2023) investigated environmentally friendly activated carbon from **banana peels** for supercapacitors, offering a sustainable alternative to hazardous processes involving graphite or fossil fuels. Characterization via FTIR, DLS, TGA, and XRD revealed the presence of hydroxyl, carbonyl, and aromatic compounds in cellulose-based carbon.

TGA confirmed complete carbonization at 700 °C. KOH activation significantly increased surface area from 553.9 m^2/g to 565.0 m^2/g BET. Specific capacitance rose from 0.3997 Fg^{-1} to 0.821 Fg^{-1}, indicating over a 100% increase, validated by cyclic voltammetry. X-ray diffraction illustrated activated carbon patterns, highlighting the feasibility of using banana peel waste for sustainable supercapacitors.

Supercapacitor-oriented activated carbons (ACs) were synthesized from ***Eucommia ulmoides*** **Oliver (EUO)** wood using a systematic activation process with H_3PO_4. By adjusting parameters, optimal ACs were obtained with a H_3PO_4 concentration of 25%, a mass ratio of feedstocks to activator at 1:4, activation time of 6 hours, and activation temperature of 400 °C. This yielded ACs with a high specific surface area (2033.9 $m^2 \cdot g^{-1}$) and predominantly well-developed mesopores (96.4%). Exhibiting outstanding electrochemical performance, the AC demonstrated a maximum specific capacitance of 252 $F \cdot g^{-1}$, a charging/discharging period of 3098.2 at 0.2 $A \cdot g^{-1}$, and a remarkable 92.3% retention rate after 10,000 cycles. This cost-effective and convenient synthesis method holds promise for widespread application in supercapacitors, particularly for utilizing EUO branches efficiently. **Su *et al.*, (2023)**

A green and sustainable renewable biomass precursor **Jujube fruit** was used to prepare hierarchical porous carbon by two step process which includes pre-carbonization at 600° C for 2h and it was activated with NaOH at 650°C for 2h which results in the formation of highly activated hierarchical structure. The obtained sample was analyzed using some characterization techniques such as SEM, HR-TEM, EDAX, TGA, XRD and XPS analysis. All the outstanding results conclude that the prepared sample would be a commercial and promising electrode material for high performance energy storage devices. **(Viengkham yang *et al.*, 2020)**

A green and freely available **mangosteen peel** waste was chosen as a biomass precursor for preparing porous carbon via a two-step process of carbonization at 600°C for 2h and activation using NaOH as an activation agent at 700°C for 2h. The synthesized porous carbon was characterized through SEM, HR-TEM, XRD, Raman spectroscopy, BET and XPS analysis. HR-TEM analysis confirmed the presence of layer like morphology. BET surface area revealed the presence of a very high BET surface area of 2,623 m^2g^{-1}. These

results prove that the prepared sample can be a promising candidate for high-performance supercapacitor **(Viengkham yang *et al.*, 2019).**

***Eucalyptus globulus* seeds** (EGS) was chosen as a green carbon precursor for preparing porous activated carbon by a simple hydrothermal method with KOH as activating agent. The prepared activated carbon was analyzed by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS) and BET techniques. The result of BET inferred that EGS activated carbon prepared at 900°C had the highest specific surface area. **(Sofia Jeniffer Rajasekaran *et al.*, 2020)**

Saccharum bengalense leaves were chosen as a biomass precursor for the synthesis of activated carbon using $ZnCl_2$ as an activating agent. The prepared activated carbon was characterized with X-ray diffraction (XRD), Field emission scanning electron microscopy, Fourier transform infrared spectroscopy (FT- IR), Raman spectroscopy and Brunauer-Emmett-Teller (BET) surface area. FTIR spectra indicated the presence of oxygen containing functional groups such as carbonyl group, hydroxyl groups and carboxyl groups. The prepared sample had a high specific surface area of 2090 m^2g^{-1} and a specific capacitance value of 102.6 F. g^{-1}. These results concluded that biomass derived activated carbon can be a good precursor for preparing electrode materials for supercapacitors**.** **(Sangeeta Rawal *et al.*, 2018)**

Figure 2.2: Biomass derived carbon materials and their applications for electrochemical energy storage

A green and environmentally friendly biomass ***Hibiscus sabdariffa*** fruit was chosen as a green carbon precursor for preparing porous activated carbon by carbonization method at 800°C for 2h and for the activation process, KOH was used. The obtained sample was characterized by using FE-SEM, TEM, XRD, Raman spectroscopy, BET and XPS techniques. TEM images depict the presence of highly porous nanosheets structure. These results conclude that increasing the carbonization temperature to 800°C increased the release of volatiles in the precursors thereby leading to enhanced development of pores and creation of new pores. **(Hamouda Adam Hamouda *et al.*, 2021)**

Wang *et al* (2013) assessed the utilisation of carbon derived from **paper pulp mill** sludge biowaste for supercapacitor applications. Paper pulp mill sludge biowaste was converted into high surface area (up to 2980 $m^2 g^{-1}$) carbon by hydrothermal carbonization followed by chemical activation. In the presence of an organic electrolyte the electrode material yielded a maximum capacitance of 166 $F.g^{-1}$ After 5000 plus charge–discharge cycles the capacitance retention was as high at 91%. The scan rate dependence of the surface area normalized capacitance highlighted the rich interplay of the electrolyte ions with pores of various sizes.

Bello *et al.*, (2016) studied the application of **pine cone biomass** derived carbon materials for supercapacitor application. Here they report on the transformation of the readily abundant pine cone biomass into porous carbon via KOH activation and carbonization at 800 °C as electrode materials for supercapacitors. The porous carbon material exhibited a mesoporous framework with a energy density of 19 W h kg^{-1}, specific surface area of 1515 $m^2 g^{-1}$ and excellent cyclability in neutral 1M Na_2SO_4 electrolyte for a symmetric carbon/carbon electrode cell. The result indicated that the material was robust and showed great promise with neutral electrolytes in high-performance energy-storage devices.

Agricultural waste, ***Allium sativum*** **peel** was utilised as a biomass precursor for preparing porous nano carbon by non-templating technique without any activation by pyrolysis method. Raw sample was characterized using TGA, FESEM, EDX, HRTEM, XRD, FTIR, Raman spectroscopy and BET techniques. TEM images highlight the presence of a spherical form of synthesized porous nano carbon. These results conclude that the

prepared sample contains abundant oxygen-containing functional groups which are responsible for conductive electrode and electrolyte interaction. **(Vinay Bhat *et al.*, 2020)**

A facile and cost-effective method was used for the preparation of nitrogen doped porous biocarbon using **Grape marcs** as a green precursor through carbonization method using urea as N-doping agent and KOH as activating agent. The obtained sample was characterized through TGA, SEM, TEM, XRD, Raman spectroscopy and XPS techniques. These results conclude that the obtained sample has large specific surface area with hierarchical porous structure and numerous N-containing groups with excellent charge storage performance. **(Zhang *et al.*, 2021)**

Naturally available biomass waste, **American poplar fruit waste**, was chosen as a carbon precursor for preparing tubular-like porous carbon via simple carbonization method at 650°C about 2h followed by an activation process using KOH as the activation agent. The prepared sample was characterized through SEM, HR-TEM, TGA, XRD, BET Raman spectroscopy and XPS analysis. These results conclude that the obtained sample of American poplar fruit waste would be an inexpensive precursor for preparing porous carbon and also a suitable electrode candidate for supercapacitor. **(Rajesh kumar *et al.*, 2020)**

Sudhan *et al.*, (2016) analysed the utilisation of Biomass-Derived Activated Porous Carbon from **Rice Straw** for a High-Energy Symmetric Supercapacitor in Aqueous and Non-aqueous Electrolytes. In this work, Biomass-derived activated carbon materials were prepared by a two-step synthesis via carbonization by KOH activation of rice straw at 600 °C in an argon atmosphere. By N_2 adsorption–desorption method the formation of disordered micro and mesopores on carbon and the high specific surface area were confirmed. Further, SEM and TEM analysis were carried out to revealed the surface morphology and aggregation of carbon nanoparticles. As a result, the promising electrode material in a supercapacitor for electrochemical energy storage and it is also feasible for commercial applications in supercapacitors.

Zhang *et al.*, (2012) estimated the preparation of activated carbon from waste ***Camellia oleifera* shell** by $ZnCl_2$ activation method for supercapacitor application. Electrochemical investigations indicate that the activated carbon (AC-3-600) obtained at the activation temperature of 600 °C and impregnation ratio of 3 shows the maximum specific

capacitance of 374 and 266 F. g^{-1} in 1 mol L^{-1} H_2SO_4 and 6 mol L^{-1} KOH electrolytes at 0.2 A g^{-1}, respectively. The high capacitance of the AC-3-600 is attributed to its high surface area (1,935 $m^2 g^{-1}$), high total pore volume (1.02 $cm^3 g^{-1}$), and especially the large percentage of micropores (735 $m^2 g^{-1}$). Meanwhile, the activated carbon presents good cycle stability in both acid and alkaline electrolytes during 5,000 cycles at a fair current density of 4 A g^{-1}. So, we had reasons to believe that the activated carbons from waste COS by $ZnCl_2$ activation might be one of the innovative carbon electrode materials for EDLCs application.

Elmouwahidi *et al.*, (2012) proposed the utilisation of activated carbon of argan **(*Argania spinosa*) seed shells** as supercapacitor electrodes. Activated carbons were prepared by KOH-activation of argan seed shells (ASS). The activated carbon with the largest surface area and most developed porosity was superficially treated to introduce oxygen and nitrogen functionalities. Activated carbons with a surface area of around 2100 m^2/g were obtained. Electrochemical measurements were carried out with a three-electrode cell using 1 M H_2SO_4 as electrolyte and Ag/AgCl as reference electrode. The O-rich activated carbon showed the lowest capacitance (259 $F \cdot g^{-1}$ at 125 mA/g) and the lowest capacity retention (52% at 1 Ag^{-1}), due to surface carboxyl groups hindering electrolyte diffusion into the pores. Conversely, the N-rich activated carbon showed the highest capacitance (355 F. g^{-1}at 125 mA/g) with the highest retention (93% at 1 A/g), due to its well-developed micro-mesoporosity and the pseudo capacitance effects of N functionalities. This capacitance performance was among the highest reported for other activated carbons from a large variety of biomass precursors.

According to **Farma *et al.*, (2013),** fibres from **oil palm empty fruit** bunches, generated in huge quantities by palm oil mills, were treated into self-adhesive carbon grains (SACG) by combining chemical and physical activation processes. The electrochemical measurements of the SACG fabricated supercapacitor cells using cyclic voltammetry, EI spectroscopy and galvanostatic charge–discharge techniques reflected that ~3 h of activation time, achieved via a multi-step heating profile, produced electrodes with a total pore volume of 0.889 cm^3g^{-1}, equivalent to high values for the specific capacitance, and specific power of 150 F g^{-1}, 4.297 Wh kg^{-1} and 173Wkg^{-1}, respectively.

A new activated carbon with high specific capacitance and low cost was prepared, employing **cotton stalk** as the raw material, by using the phosphoric acid (H_3PO_4) chemical activation method. The specific surface area and pore volume of activated carbon were calculated by Brunauer–Emmett–Teller (BET) and t-plot methods. With these experimental conditions, an activated carbon with a micropore volume of 0.0377 $cm^3 g^{-1}$and BET surface area of 1,481 $cm^2 g^{-1}$ was obtained. The capacitance of the prepared activated carbon was as high as 114 $F g^{-1}$. The results indicate that cotton stalk can produce activated carbon electrode materials with low cost and high performance for electric double-layer capacitor. **Chen *et al.*, (2013)**

Liang *et al.*, (2014) examined a honeycomb-like porous carbon derived from **pomelo peel** for use in high-performance supercapacitors. Here they reported the preparation of a three-dimensional (3D) honeycomb-like porous carbon (HLPC) by a simple carbonization followed by KOH activation. Structural characterization indicated that the as-prepared HLPC with a high specific surface area (SSA) up to 2725 $m^2 g^{-1}$.

Qu *et al.*, (2015) proposed that biowaste **corncob residue** may be used as a precursor to prepare porous carbon by one-step activation without pre-carbonization. After the ash removal, porous carbon achieved a high surface area of 1210 m^2g^{-1}. The carbon electrode exhibited a high capacitance of 314 F g^{-1} in 6 M KOH electrolyte and had excellent cycling stability even after 100,000 cycles. According to the authors, the excellent electrochemical performance was due to the combination of a high specific surface area with a fraction of mesopores and highly stable structure.

Misnon *et al.*, (2015) investigated the electrochemical properties of activated carbon derived from **oil Palm kernel shell (PKS)** for fabricating high performance electrochemical double layer capacitors. By pyrolysis method cleaned PKS were carbonized and subsequently activated by physical and chemical methods. Galvanostatic tests indicated that the electrodes maintained 95–97% of CS after 1000 cycles. The results shows that the electrochemical properties of the two types of AC are evaluated using electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge cycling in three-electrode system.

According to **Wang *et al.*, (2015) ,** activated carbon particles interconnected into 3D micrometre-level large pores were prepared from a novel biomass named **willow**

catkins (WCs) by KOH chemical activation process and used as electrode materials for supercapacitors. The supercapacitors with the carbon electrode reached maximal specific capacitances of 340 F g^{-1} and high specific surface capacitance of 52.7 μF cm−2 at the current density of 0.1 A g^{-1}, good rate capability (231 F g^{-1} at 10 A g^{-1}) and good cycling stability (92% capacitance retention over 3000 cycles). The favourable capacitive performances make the waste biomass WCs act as a new resource of carbonaceous materials for high performance supercapacitors.

Hierarchical porous activated carbon for supercapacitor derived from **corn stalk core** by potassium hydroxide activation for Supercapacitor application. By the activation of corn stalk core (CSC) using potassium hydroxide at 700 °C the high specific surface area of the activated carbon (AC) was produced. SEM, TEM and XRD analysed the microstructure and crystallographic orientation of the carbon samples. Based on CSC-700CV, galvanostatic charge/discharge and electrochemical impedance spectroscopy were measured. A specific capacitance of 323 F g^{-1} in 6 mol L^{-1} KOH electrolyte was obtained at a current density of 0.1 A g^{-1}, and it still maintained very good cyclic stability with capacitance retention ratio of 97.9% at current density of 1.0 A g^{-1} for 1000 cycles. **Cao *et al.*, (2016)**

Qin *et al.*, (2016) estimated the performance of **Pomegranate rind-derived activated carbon** as electrode material for supercapacitor application through carbonization and alkaline activation processes. At different pyrolytic temperatures the surface area of the activated carbon can reach at least 2200 m^2 g^{-1}. It was found that, at the range of 600–900 °C, decreasing the carbonization temperature led to the increase of t-plot micropore area, capacitance and t-plot micropore volume. Further decreasing the carbonization temperature to 500 °C also leads to the increase of t-plot micropore area and t-plot micropore volume, but the capacitance is slightly poorer. The activated carbon carbonized at 600 °C and activated at 800 °C possesses very high specific area (2931 m^2 g^{-1}) and exhibits very high capacitance. There is no capacitance fading after 2000^{th} cycle.

Rajagopal *et al.*, (2016) tested the activated carbon derived from non-metallic **printed circuit board** (PCBs) waste for supercapacitor application. Activated carbons (ACs) have been synthesized by using waste PCBs via physical activation

following to pyrolysis processes. The physical and chemical properties of the produced activated carbons were studied using nitrogen adsorption, SEM, FT-IR, RAMAN spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy . Among the synthesized activated carbon with the highest surface area of 700 $m^2 g^{-1}$ produced at 850 °C for a time interval of 5 h was subjected to electrochemical studies. Capacitance behaviour of the obtained AC sample has been evaluated using Cyclic Voltammetry (CV), Galvanostatic Charge–Discharge (GCD) measurements and electrochemical impedance spectroscopy (EIS) technique. Specific capacitance (C_{sp}) values vary from 156, 185 and 220 F g^{-1} for the scan rate of 100, 50 and 30 mV s^{-1}respectively. The well-developed surface area properties and good capacitance values associated with nitrogen functionalities indicates the AC developed is a suitable and good candidate for the supercapacitor fabrication.

Porous carbons were prepared by simple carbonization of **green onion leaves** at temperatures from 600 to 800 °C and were employed as electrode materials of supercapacitors. TGA, XRD, EDX, SEM, FESEM, AAS and nitrogen adsorption were used to characterize their morphology, surface elemental composition and pore structure. CV, CD and Impedance were carried out to evaluate their specific capacitance, resistance and cycling life. Results showed that during the carbonization process the initial mineral elements present in the leaves such as calcium (Ca) and potassium (K) plays an activating role. The effective areal capacitance of the carbon prepared at 800 °C was found to be higher than of most porous carbons described in the literature, which might be ascribed to its pore size distribution that favoured ion access to its pores. **Yu *et al.*, (2016)**

Xuan *et al.*, (2017) investigated the preparation of biomass-activated porous carbons derived from ***Torreya grandis* shell** for high-performance supercapacitor. In this paper, they reported a novel biomass-derived porous carbon from *Torreya grandis* shell by means of carbonization and KOH activation under N_2. The pore structures were related to the ratio of KOH and activation temperature. N_2 adsorption-desorption tests indicated that the sample of AC-800-3 has a maximum specific surface area of 2100.8 $m^2 g^{-1}$and proper pore volume of 1.02 $cm^3 g^{-1}$. The electrode prepared with AC-800-3 realized a high capacitance of 290.5 F g^{-1} at 0.5 A g^{-1} and excellent rate capability of 62.6% in three-electrode system. The assembled symmetrical cell of AC-800-3 electrode exhibited a high

energy density of 13.5 W h kg^{-1} at a power density of 360.1 W kg^{-1} in the potential range of 0-1.6 V and excellent cycling stability with 93.1% retention of the initial capacitance after 5000 cycles.

Taer *et al.*, (2017) investigated seven types of activated carbon electrode (ACM) from **banana peel waste** for supercapacitor application. The specific surface area (SBET), Csp, E and P were found to have a maximum value of 581m^2 / g, 68 F/g, 0.75 Wh/kg and 31 W/kg, respectively. Furthermore, this paper was also analysed the relationship between electrochemical properties of supercapacitor with the degree of crystallization of the ACM.

Ma *et al.*, (2018) examined a facile approach to prepare biomass-derived activated carbon hollow fibres from **wood waste** as high-performance supercapacitor electrodes. In this paper, from wood waste several activated carbon hollow fibres (ACHF) were prepared by liquefaction, one-step activation and half-curing methods. SEM, Nitrogen gas adsorption–desorption and X-ray photoelectron spectroscopy were used to characterize the structural morphology and composition of ACHF.

Ahmed *et al.*, (2018) evaluated the Supercapacitor performance of activated carbon (AC) derived from **rotten carrot** in aqueous, organic and ionic liquid-based electrolytes. AC was derived from rotten carrot, at various activating temperature under inert atmosphere, by chemical activation method and $ZnCl_2$ as activation agent. Morphology, thermal stability, and crystal structure of prepared AC were studied using standard techniques of material characterization. By using organic and ionic liquid-based electrolyte it was found that the synthesized AC based electrode exhibits highest specific capacitance in aqueous electrolyte and highest specific energy and specific power in ionic liquid-based electrolyte. This shows the suitability of synthesized material for use in energy storage applications.

Ahmed *et al.*, (2018) analysed on an activated carbon derived from neem **(*Azadirachta indica*),** and its application as supercapacitor electrode. They reported the preparation of quasi solid-state supercapacitor employing activated carbon (AC) electrodes and gel polymer electrolyte (GPE).AC was derived from Neem leaves by chemical activation using zinc chloride. GPE was prepared using solution-cast technique and

comprises of $LiClO_4$ salt, dispersed in EC: PC (1:1 vol.) and entrapped in PVDF-HFP solution. AC was characterized by SEM, TEM, XRD, Raman spectroscopy, TGA and BET tests while GPE was characterized by (ESW) and conductivity test. These results demonstrate the suitability of prepared AC as promising electrode material for supercapacitor applications.

Liu *et al.*, (2018) inspected the utilisation of activated carbons derived from **soybean pods** as electrode materials for high-performance supercapacitors. The authors inferred that the resulting carbon activated by KOH possessed richer textural properties than the one activated by $ZnCl_2$. With abundant micro-, mesopores and interconnected macropores, the KOH-activating carbon was found to possess a specific surface area up to 2245 $m^2 g^{-1}$ and a large pore volume of 1.35 $cm^3 g^{-1}$. In a three-electrode system, the KOH-activating carbon delivered a high specific capacitance of 321.1 F g^{-1} at a current density of 1 A g^{-1}in 6 M KOH aqueous electrolyte. When used as symmetric electrode in 1 M Na_2SO_4 neutral aqueous solution, the SPAC−K/SPAC−K supercapacitor provided a high energy density up to 22.3 Wh kg^{-1} at a power density of 450 W kg^{-1} in a wide voltage window of 0–2.0 V, surpassing most of the previously reported waste biomass-based carbon materials. The impressive electrochemical performances as well as the low-cost scalable production manifest that the SPAC−K derived from waste soybean pods can be a promising electrode candidate for supercapacitor application.

A green and sustainable biomass precursor **Baobab fruit shell** was used to prepare activated carbon through the carbonization process at 800°C for 3h and it was activated by using KOH and H_3PO_4. The obtained samples were analyzed by using SEM, XRD, Raman spectroscopy and XPS techniques. These results conclude that the obtained samples contain hierarchical porous carbon, in which the KOH activated sample contain honeycomb-like structure with a high specific surface area of 1059 m^2g^{-1} and H_3PO_4 activated sample contain spherical carbon with high specific surface area of 991.7 m^2g^{-1} and it was a suitable electrode material for high performance supercapacitor **(Asim Mohammed *et al.*, 2018).**

A green and environmentally friendly biomass precursor, **Pueraria**, the root of Kudzu, was used to prepare nitrogen-doped porous activated carbon by two steps. Firstly, *Pueraria* powder and melamine were fully mixed and hydrothermally treated, followed by pyrolysis and activation using K_2CO_3. The prepared sample were studied using SEM, TEM,

XPS and XRD techniques. The prepared sample exhibited a high BET surface area of 2321 m^2g^{-1} with 99% small size mesoporous structure and it is a promising electrode material for supercapacitors **(Xiuli Han *et al.*, 2018).**

Zhang *et al.*, (2018) proposed the synthesis of **garlic skin**-derived 3D hierarchical porous carbon with KOH as the activating agent for high-performance supercapacitors. Due to its unique interconnected porous structure, this garlic skin-derived carbon shows excellent cycling stability and electrochemical performance. At a current density of 0.5 A g^{-1}, the capacitance is up to 427 F g^{-1} (162 F cm^{-3}). The results shows that garlic skin-derived 3D hierarchical porous carbon is a promising electrode material for high-performance supercapacitors.

Lotus leaf, a renewable source of biomass, was successfully explored as a low-cost crude carbon source for preparing high-value lotus leaf porous carbon(LLPC) via carbonization and KOH activation. At a current density of 20 A g^{-1}, the specific capacitance reached as high as 298 F g^{-1}. Furthermore, after 5000 charging/discharging cycles, the capacitance retention rate was 90%. When the energy density of the electrode was 9.2 W h kg^{-1}, the power density was 491 W kg^{-1}. The achieved electrochemical performance demonstrated that lotus leaves can function as a new biomass material for the production of high-performance supercapacitors and low-cost energy storage devices. **Qu *et al.*, (2018)**

A low cost, renewable and sustainable biomass **willow wood (*Salix sp.*)** was chosen as a green carbon precursor for preparing activated carbon by carbonization at 600° C followed by chemical activation using KOH at 800°C. The prepared sample was studied using SEM, Raman spectroscopy and XPS techniques. These results prove that the obtained activated carbon has high surface area and high pore volume with a unique combination of micropores and mesopores with excellent electrochemical performance **(Josphat Phiri *et al.*, 2019).**

2.2.2. Industrial Waste as Carbon Sources

The utilization of industrial waste as carbon sources for supercapacitor applications has gained significant attention due to its environmental and economic benefits. Various

studies highlight the potential of converting different types of industrial waste into high-performance carbon materials suitable for supercapacitor electrodes.

Oil shale semi-coke (OSS), a major byproduct of oil shale pyrolysis, poses environmental challenges due to its large-scale production. Addressing this issue, a study by **Xiong *et al.*, (2023)** explored the sustainable and effective utilization of OSS by transforming it into activated carbon through microwave-assisted separation and chemical activation for supercapacitor applications. Characterization techniques, including Raman, XRD, FT-IR, TEM, and nitrogen adsorption–desorption, disclosed that ACF activated with $FeCl_3$-$ZnCl_2$/carbon precursor exhibited a larger specific surface area, suitable pore size, and higher graphitization compared to other methods. Electrochemical assessments demonstrated a specific capacitance of 185.0 $F.g^{-1}$ at 1 Ag^{-1} and a remarkable capacitance retention rate of 99.5% after 5000 cycles. This approach provided a promising strategy for converting waste OSS into low-cost activated carbon materials for high-performance supercapacitors.

Lee *et al.*, (2011) examined the feasibility of utilising **Beer lees** precursor to prepare activated carbons having different chemical and physical properties. The beer lees-based activated carbons were characterized by X-ray photoelectric spectroscopy, N_2 adsorption/desorption isotherms and adsorption energy distributions. The results of electrochemical properties of the BL-ACs were performed using CV, EIS and charge/discharge method were evaluated. The results demonstrated that in 0.1M H_2SO_4 electrolyte solution, a maximum specific capacitance about 188 F/g at discharge current of l mA/cm^2 was obtained. The overall results recommend that the BL-ACs acted as excellent electrode materials as electric double layer capacitors.

One notable study demonstrated the conversion of **furfural residue**, a common industrial waste, into high-performance carbon materials for supercapacitors. The method involved methanol pretreatment, pre-carbonization, and KOH activation. The resulting carbon materials exhibited excellent electrochemical performance and a high specific surface area of 1753.5 m^2/g **(Guo *et al.*, 2022)**.

Industrial wastes, such as **apple pulp, cherry stones**, and polyethylene terephthalate (PET), have been recycled into activated carbons for supercapacitors. These materials were

found to offer high specific surface areas and electrical capacitances of up to 230 F/g in 2M H_2SO_4 aqueous electrolyte and 120 F/g in aprotic medium **(Centeno *et al*., 2022)**.

Meng *et al*., 2019 effectively transformed **cigarette butt** waste into nitrogen-doped carbon, exhibiting excellent specific capacitance, good rate performance, and high cycling stability. This approach not only addresses environmental issues related to cigarette waste but also produced high-performance materials for supercapacitors

Glycerine waste was utilized as a sustainable precursor for producing activated carbons with potential applications in supercapacitors. These materials show high specific capacitance and adsorption capacities for organic contaminants, such as paracetamol and methylene blue **(Gonçalves *et al*., 2019)**.

The transformation of discarded masks into high-performance activated carbon materials for supercapacitors was demonstrated by **Yu *et al*., 2023**. This process not only addressed the growing environmental concern of **mask waste** but also produces materials with high specific capacitance suitable for advanced supercapacitors

Graphitic carbon nitride (g-CN) and g-CN/carbon hybrids synthesized from synthetic waste displayed favorable electrochemical properties for electrode fabrication in supercapacitors. These materials demonstrate the potential of utilizing synthetic industrial waste for energy storage applications **(Devi *et al*., 2023)**.

The utilization of industrial waste as carbon sources for supercapacitor applications offer a dual benefit of mitigating environmental pollution and providing cost-effective materials for energy storage. Various types of industrial waste, including furfural residues, apple pulp, cherry stones, PET, cigarette butts, glycerin waste, discarded masks, and synthetic waste, have been successfully converted into high-performance activated carbon materials. These efforts highlight the potential of industrial waste-derived carbon materials in advancing sustainable and efficient supercapacitor technologies.

2.2.3. Marine Waste as carbon

The use of marine waste as carbon sources for supercapacitor applications is an emerging field that combines environmental sustainability with advanced energy storage

solutions. Various types of marine waste have been successfully converted into high-performance activated carbon materials for supercapacitors, showcasing their potential as cost-effective and eco-friendly alternatives to traditional carbon sources.

Shrimp shell waste was converted into porous activated carbon through chemical activation methods. The resulting materials exhibit high specific capacitance and excellent electrochemical stability. For instance, shrimp shell-derived carbon demonstrated a specific capacitance of up to 225 F/g at 1 A/g in NaOH electrolyte, making it a promising candidate for low-cost, scalable supercapacitors
(Nanda *et al*., 2022).

Fish scales, another abundant marine waste, were explored as a carbon source for supercapacitors. The scales, rich in collagen, was carbonized and activated to produce porous carbon materials. These fish scale-derived carbons have shown high surface areas and good electrochemical performance, providing a sustainable alternative for energy storage applications **(Nanda *et al*., 2022)**.

Algae, an abundant and renewable marine resource, was converted into high-performance carbon materials for supercapacitors. The process typically involves pyrolysis and activation of algae biomass to produce porous carbon with a high surface area. Algae-derived carbons have demonstrated excellent electrochemical properties, including high specific capacitance and good rate capabilities, making them suitable for use in supercapacitors **(Sundriyal *et al*., 2021)**.

Seaweed, another marine biomass, was utilized to produce activated carbon for supercapacitors. The carbonization and activation of seaweed biomass result in porous carbon structures with good electrical conductivity and capacitance. Seaweed-derived carbons offer a sustainable and renewable source for high-performance supercapacitor electrodes **(Nanda *et al*., 2022)**.

Crab shells, similar to shrimp shells, contain chitin and proteins that can be transformed into activated carbon. The activation process involves treating the crab shells with chemical agents like KOH or $ZnCl_2$, followed by carbonization. The resulting carbon

materials exhibit high porosity and surface area, contributing to their high electrochemical performance in supercapacitors **(Meng *et al.*, 2023)**.

The use of various marine wastes as carbon sources for supercapacitor applications provides an innovative and sustainable approach to waste management and energy storage. Shrimp shells, fish scales, algae, crab shells, seaweed, and oyster shells have all been successfully converted into high-performance carbon materials. These materials demonstrate excellent specific capacitance, high surface area, and good electrochemical stability, making them suitable for advanced supercapacitor applications. This approach not only addresses the environmental issue of marine waste disposal but also contributes to the development of cost-effective and eco-friendly energy storage solutions.

2.2.4. Nitrogen doped biomass carbon

Shu *et al.*, (2017) investigated Nitrogen-doped porous monolithic carbon (NDPMC) is obtained from biomass-derived activated carbon/polyacrylonitrile composite for the first time via a template-free thermally induced phase separation (TIPS) approach followed by KOH activation. The electrochemical results indicate that NDPMC possessed ultrahigh specific capacitance of 442 F g^{-1} at 1 A g^{-1}, excellent rate capability with 81% retention rate from 1 to 100 A g^{-1} and outstanding cycling stability with 98% capacitance retention at 20 A g^{-1} after 5000 cycles. Furthermore, the evaluation of NDPMC on the practical symmetrical system also exhibited desired electrochemical performances.

Xuan *et al.*, (2017) reported a simple synthetic method to fabricate nitrogen doped porous carbon (NPC) via a one-pot carbonization of sodium alginate and urea. The as-prepared NPC annealed at 700 °C with meso- and macro-porous structure exhibited excellent specific capacitance (180.2 F/g at 1 A/g) and superior cycling life when serves as electrode materials for supercapacitor. Moreover, the investigation on the annealing temperature demonstrated that NPC pyrolysis at 700 °C possessed relatively high pyrrole nitrogen and pyridine nitrogen, which might be favourable for enhancing supercapacitor performance.

Du *et al.*, (2018) investigated the use of celery as a biomass carbon precursor to prepare nitrogen-doped hierarchical porous carbon materials by activation, polymerization

and carbonization. Prepared Celery-derived activated carbon was utilized to synthesize activated carbon/polyaniline composite material by wet-chemistry method and further carbonized to obtain nitrogen-doped hierarchical porous carbon. The nitrogen-doped hierarchical porous carbon materials were found to exhibit high specific capacitance of 402 F g^{-1} in 1 M H_2SO_4 electrolyte at 1 A g^{-1}. After 10,000 GCD cycles, material displayed an impressive cycling stability of 97% capacitance retention. The outstanding electrochemical performance endowed nitrogen-doped hierarchical porous carbon with enormous prospects as a supercapacitor electrode material.

Boron and nitrogen (B/N) co-doped carbon nanospheres were successfully prepared by emulsion crosslinking method using chitosan and boric acid as raw materials. Applying the carbon nanospheres for supercapacitors, **Yang *et al.*, 2022** reported that the specific capacitance reached up to 336.7 F g^{-1} at a current density of 1 A g^{-1}. Even after 10,000 cycles, the Coulomb efficiency and specific capacitance remained at 98.6% and 96.8%, respectively, demonstrating the great promise of B/N co-doped carbon nanospheres for the state-of-the-art supercapacitor electrodes applications**.**

Bio-waste (oil extracted from eucalyptus leaves) was used as a carbon precursor to synthesize carbon material with $ZnCl_2$ as a chemical activating agent and activated carbon was synthesized at various temperatures ranging from 400 to 800 °C. The activated carbon at 700 °C exhibited a surface area of 1027 m^2 g^{-1} and a specific capacitance of 196 F g^{-1}. In order to enhance the performance, activated carbon was doped with nitrogen-rich urea at a temperature of 700 °C. The obtained activated carbon and N-doped activated carbon was characterized by phase and crystal structural using (XRD and Raman), morphological using (SEM), and compositional analysis using (FTIR). The electrochemical measurements of carbon samples were evaluated using an electrochemical instrument and NAC-700 °C exhibited a specific capacitance of 258 F g^{-1} at a scan rate of 5 mV s^{-1} with a surface area of 1042 m^2 g^{-1}. Thus, surface area and functionalizing the groups with nitrogen showed better performance and it can be used as an electrode material for supercapacitor applications **(Bejjanki *et al.*, 2023)**.

2.3. Factors affecting specific capacitance

The capacitance of supercapacitors, also known as electric double-layer capacitors (EDLCs), is influenced by various factors that play a crucial role in their performance. Understanding these factors is essential for optimizing the capacitance and overall efficiency of supercapacitor devices.

- One significant factor is the surface area of the electrodes. In supercapacitors, the electrodes are typically made of porous materials with a high surface area. The greater the surface area, the more electrode-electrolyte interface is available for charge storage, leading to increased capacitance.
- Another important factor is the nature and properties of the electrolyte used. The choice of electrolyte affects the charge transfer process and ion mobility within the supercapacitor. Different electrolytes can have varying ion sizes, solvation properties, and conductivity, which in turn impact the capacitance of the device.
- The electrode material composition also influences the capacitance. Carbon-based materials, such as activated carbon and carbon nanotubes, are commonly used due to their high conductivity and large surface area. The presence of functional groups or doping can further enhance the capacitance by modifying the surface chemistry and altering the charge storage mechanisms.
- Electrode thickness and porosity are additional factors that affect the capacitance. Thicker electrodes provide more space for ion diffusion and storage, increasing the capacitance. Likewise, a higher porosity allows for better electrolyte penetration and ion accessibility, enhancing the charge storage capacity.
- Furthermore, the operating voltage or potential window applied to the supercapacitor affects its capacitance. The capacitance can vary at different voltage ranges due to changes in the charge storage mechanism and the degree of ion adsorption/desorption at the electrode-electrolyte interface.

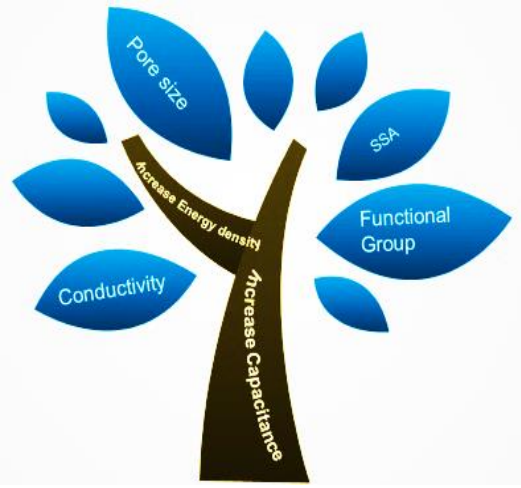

Figure 2.3: Essential elements affecting capacitance.

In summary, factors such as electrode surface area, electrolyte properties, electrode material composition, thickness, porosity, and operating voltage all contribute to the capacitance of supercapacitors. Optimizing these factors enables the design and development of high-performance supercapacitor devices with improved energy storage capabilities (**Wu & Cao 2018).**

2.3.1. Effect of pore size and SSA

The scientific community has analysed the usage of porous materials on electrodes to improve the electrochemical performance of energy storage devices. According to the EDLC process, the high specific surface area of carbon materials generates a larger electrode/electrolyte interface for ion adsorption, thus improving the capacitance **(Wang *et al.*, 2016)**. Additionally, the electrochemical performance of carbon materials is affected by their pore size distribution, pore structure, and connectivity, all of which influence ion and electron transport **(Frackowiak 2007)**. The specific surface area of carbon nanoparticles has been reported to be high for conventional electrode materials. In general, the charge accumulation capability of carbon increases with the specific surface area **(Chmiola *et al.*, 2006**). The International Union of Pure and Applied Chemistry (IUPAC) classifies porous materials into three categories based on pore size. These are microporous materials with pore sizes smaller than 2 nm, mesoporous materials with pore sizes ranging from 2 nm to 50 nm, and macroporous materials with pore sizes larger than 50nm **(Xia *et al.*, 2010).**

Several significant reasons explain why porous materials are used in SCs: They are capable of varying pore sizes because of their high surface areas and ability to facilitate ion diffusion and storage in SC electrodes, and chemical activation followed by pyrolysis has been reported to be an effective method for the formation of pores in carbon materials **(Mendoza *et al.*, 2022)**. To construct supercapacitors, electrode materials are the most critical components. Porous carbon materials, particularly those derived from biomass, are commonly used for this purpose **(Bi *et al.*, 2019**) Porous carbon materials have unique physical and chemical properties, such as a high surface area, large pore volume, and tuneable pore size, which enable them to store and transport charge more efficiently.

By rationally constructing and developing these materials, their potential for use in supercapacitors can be maximized, thereby allowing for greater charge storage and transport. Supercapacitors need to be optimized and regulated in order to deliver dependable performance in real-world applications, even though many researchers have published intriguing results on a lab scale. A hierarchical porous structure is highly desired because the electrode material of the supercapacitors acts as a route for charge transfer during the electrochemical process. In electrochemical charging and discharging processes, different pores have distinct functions **(Sun *et al.*, 2022, Liu *et al.*, 2017, Xie *et al.*, 2020)**. To reduce the ion diffusion distance, macropores serve as massive ion buffer cells. Short-range mesopores have a remarkable rate capacity and power density because they offer a low-resistance channel for rapid ion transmission to the electrode's interior space (**Xie *et al.*, 2020, Bokhari *et al.*, 2020)** As they offer many active sites for ion storage and mass diffusion, as well as enhancing the EDLC, micropores are thought to be the most efficient size for ion accumulation **(Wang *et al.*, 2020)**.

Li *et al.*, (2020) reported that in order to increase the energy density of supercapacitors without compromising their high-power densities, large micropores with pore sizes of 1-2 nm are needed as they provide high charge storage ability while ensuring quick ions transportation.

Owing to its obtainability, renewability, low cost, and eco-friendliness, biomass is regarded as a key raw material for the construction of carbon-based energy storage technologies **(Bi *et al.*, 2019**). Porous carbons with high capacitive qualities have been produced using a variety of biomasses, including Cycas fluff **(Xiao *et al.*, 2022)**, walnut peel **(Xu *et al.*, 2021)**, mangosteen peel **(Khajonrit *et al.*, 2022)**, and wheat husk **(Wang *et al.*, 2022)**. Although traditional pyrolysis carbonization produces porous carbons with high specific surface areas, hierarchical pore structures, and good surface wettability, porous carbons made from biomass have poor conductivity, which leads to insufficient capacitance retention under high current densities. By using Iron, Cobalt, and Nickel as catalysts in the biomass pyrolysis, graphitized porous carbon with high electrical conductivity can be synthesized **(Wang *et al.*, 2016, Xie *et al.*, 2014, Hoekstra *et al.*, 2015).** An increase in the degree of graphitization degrades the porous structure of carbon materials, resulting in a

significant decrease in the specific surface area, which ultimately affects the storage capacity of porous carbon **(Xie *et al.*, 2014)**. **(Gong *et al.*, 2017)** augmented that micro pore structures with pore size less than 1 nm were highly ineffective in rapid transportation of electrolyte ions. **(Li *et al.*,2020)** suggested that huge micropores can assure great charge storage capability while enabling quick ions movement. Consequently, it is expected that porous carbons formed from biomass will have a high degree of graphitization, good surface wettability, and an optimized pore size distribution, which will enable them to operate at high rates even when exposed to extremely high current densities. The relationship between pore size, pore volume, SSA and capacitance for few biomass materials have been tabulated in Table 2.1.

Table 2.1: Relationship between pore size, pore volume, SSA and capacitance for few biomasses materials

Material	SSA m^2/g	Pore volume	Nature of pore	Capacitance F/g	References
Flaxseed residues	3326 3230 1976	1.56 1.67 1.00	Micropore	345 369 273	**Li *et al.*,2020**
Ganoderma lucidum residues	1347	0.87	-	365	**Xu *et al.*, 2021**
Mangosteen peel	1039	0.635	Micropore	182	**Khajonrit *et al.*, 2022**
Walnut peel	2495	1.339	Micropore	557	**Xu *et al.*, 2021**
Phoenix fallen leaves	1352 2208 1024	0.80 1.27 0.87	Micropore, mesopore	61.1 53.5 17.1	**He *et al.*, 2020**
Wheat husk	2721 2202 1739	1.66 1.41 1.01	Mesopore	402 210 199	**Wang *et al.*, 2022**
Cycas fluff	516.70	0.33	Micropores, meso /macropores	349	**Xiao *et al.*, 2022**
Peanut shell K_2CO_3- AC KCl-AC KOH-AC NaOH-AC	1260.65 886.95 2936.8 2556.15	0.65 0.47 1.53 1.41	Micropore, mesopore	250 210 339 284	**Gopalakrishnan & Badhulika (2021)**

Material	SSA m^2/g	Pore volume	Nature of pore	Capacitance F/g	References
Activated carbon from Bamboo. BC 700 ABC 700 ABC 800 ABC 900 ABC 1000	 674.3 1028.6 2133.3 2221.1 2715.1	 0.382 0.599 1.273 1.238 1.509	mesoporous	 97.5 156 169.2 293 253	**Han *et al.*, 2018**
Activated carbon from walnut shell	1016.4 938.9 728.2	0.56 0.61 0.45	micropore	156.19 138.15 109.76	**Lan *et al.*, 2013**
Bamboo based activated carbon	915 930	1.05 0.66	mesoporous, macroporous	225 209	**Zheng *et al.*, 2022**
Pinecone biomass	1515	0.38	mesoporous, microporous	137	**Bello *et al.*, 2018**
Lotus leaf LLPC-700 LLPC-800 LLPC-900	 2297 2489 2488	 0.98 1.14 1.28	mesoporous, microporous	 344 379 286	**Qu *et al.*, 2016**
Natural bamboo BC PBC1 PBC2	 4 257 1732	 0.01 0.36 0.97	microporous	 111 171	**Gong *et al.*, 2017**
Activated carbon from Bamboo Activated carbon from Sugarcane Bagasse Activated carbon from orange peels	 1273 1069 915	 0.61 0.53 0.51	microporous	 498 486 145	**Shetty Ajay *et al.*, 2022**
Pueraria	2321	1.26	mesoporous	250	**Han *et al.*, 2018**
Rubber Seed Shell	148	0.048	mesoporous, microporous	123	**Kanjana *et al.*, 2021**
Durian Shell	180	0.093	mesoporous, microporous	178	
Palm Petiole	436	0.241	mesoporous, microporous	177	

Material	SSA m^2/g	Pore volume	Nature of pore	Capacitance F/g	References
Untreated bagasse	3135	1.39	mesoporous	410	**Tan *et al.*, 2021**
Pomelo peel	1626	0.85	microporous	317	**Wang *et al.*, 2019**
Bamboo fiber	1450	0.70	microporous	286	
Sugarcane bagasse	2206	1.12	microporous	255	
Hibiscus sabdariffa fruits HBFC-1 HBFC-2 HBFC-3 HBFC-4	 1720 1711 377 23.54	 0.863 1.050 0.198 0.047	Micropores, meso /macropores	194	**Hamouda *et al.*, 2021**
Coconut shells CSC CSCK1, CSCK2, CSCK3	 287 1178 1567 1336	 0.11 0.68 0.69 0.61	Micropores, meso /macropores	449	**Lee *et al.*, 2021**

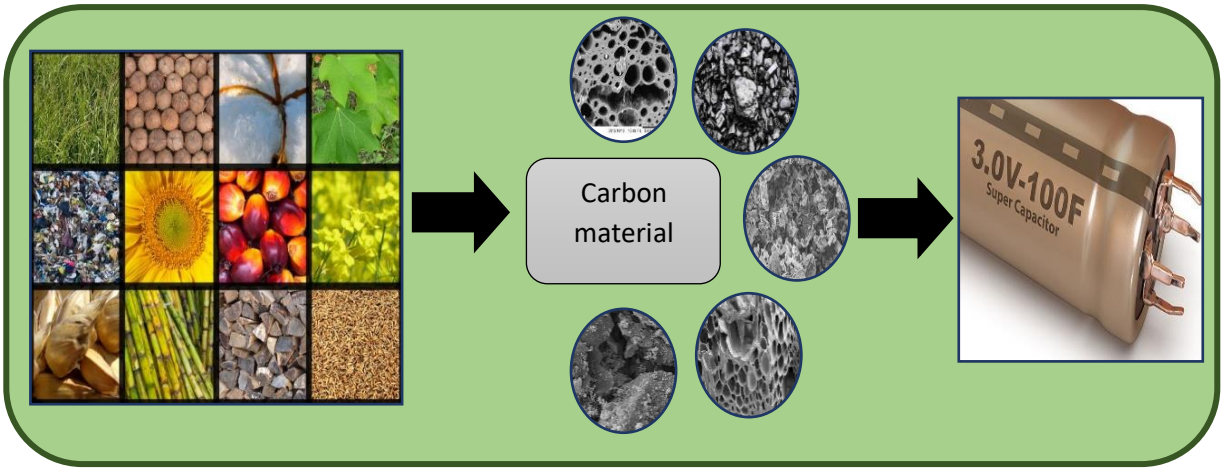

Figure 2.4: Schematic diagram represents the usage of various biomass as an electrode for energy storage device.

(Li *et al.*, 2019) investigated that large micropore (1 nm < d < 2 nm) dominant microporous carbon was reported with more than 70.1% of micropore volume contributed by the large micropores. Specific capacitance reaches 369 and 398 F g^{-1} in KOH and H_2SO_4 electrolyte, respectively. Excellent rate and cycle performance were observed, with a high energy density of 61.2 Wh kg^{-1} in ionic liquid.

2.3.2. Effect of binders on capacitance

The binder should offer sufficient strength during electrode formation and suitable pore sizes. However, cohesive agents and binders invariably cover some of the surface areas or pores of the active materials. Consequently, the electrochemical performance of supercapacitors is directly influenced by the characteristics of the binders and their contents in the electrodes. Therefore, the selection and optimization of the binder are crucial for developing high-performance electrodes for supercapacitors **(Zhu *et al.*, 2016)**. The main purpose of the binder is to provide sufficient strength during electrode construction and appropriate pore diameters. The amount of binder should be minimized as much as possible to prevent degradation of the surface area or conductivity of the electrode **(Ruiz *et al.*, 2007)**. However, binders fill some of the pores or surface areas of the active materials, obstructing the channels that ions use to travel through the pores. It is necessary to establish the association between the amount of binder employed during preparation and the pore size distribution, as well as how these factors affect the electrochemical characteristics of the electrode. Therefore, a comprehensive understanding of the role of the binder in electrode fabrication is essential for designing high-performance electrodes **(Abbas *et al.*, 2014)**. To maintain the integrity of electrodes during electrochemical operation, two types of binders, poly(tetrafluoroethylene) (PTFE) and poly (vinylidene difluoride) (PVDF), have been used indifferently.

Zhentao Zhu *et al.*, (2014) evaluated the performance of Nafion, PTFE, and PVDF-based AC electrode materials. The PTFE-based electrode was found to perform better than the other two, and the ideal proportion of the three binders in the electrode material was determined. In addition to having a high specific capacitance, an excellent binder must have good adhesive properties and exceptional thermal, chemical, and electrochemical stability for exceedingly long cycles.

To ensure maximum performance and reliability, an ideal binder should be able to endure regular charge and discharge cycling without any signs of deterioration. An electrochemically active material with nanostructured and porous graphene structures that have large SSAs can increase the contact between the electrode and the electrolyte, resulting in a significant decrease in the diffusion resistance, and graphene networks formed by stacking or connecting graphene can significantly improve the conductivity and reliability without the addition of inactive binders. Binder-free electrodes with typical free-standing structures can reduce the total weight of the devices by eliminating the need for a metal current collector. They can also be used as flexible electrodes **(Ji *et al.*, 2015)**. Table 2.2 indicates the relation between type of binder, binder ratio and Csp.

Table 2.2: Relation between type of binder, binder ratio and Csp

Active material	Binder	Ratio [AM: CM: B]	Operating Voltage (V)	Electrolyte	Capacitance (F/g)	References
Ganoderma lucidum residues	PTFE	8:1:1	−1.0 to 0	6M KOH	365	**Xu *et al.*,2021**
Peanut shell based activated carbon	PTFE	8:10:10	-1 to 0	6M KOH	339	**Zhan *et al.*,2021**
Onion skin	PVDF	8:1:1	0 to1.4	1M Na_2SO_4	478	**Gopalakrishnan *et al.*,2021**
Bamboo	PTFE	80:10:10	-1 to 0	3M KOH	293	**Zhang *et al.*,2018**
(O, N)-doped porous carbon derived from bamboo shoots shells	PTFE	80:15:5	0 to 1.0	1M H_2SO_4	223	**Han *et al.*,2018**
Walnut shell	PTFE	8:1:1	0 to1	6 M KOH	162	**Lan *et al.*,2020**
Dead neem leaves	PVP	80:15:5	0 to1	1M H_2SO_4	400	**Biswal *et al.*,2013**
Bamboo based activated carbon	PTFE	70:20:10	−0.2 to 0.8	1M H_2SO_4	225	**Zheng *et al.*,2022**
Osmanthus	PTFE	8:1:1	-1 to 0	3M KOH	351	**Li *et al.*,2021**

Active material	Binder	Ratio [AM: CM: B]	Operating Voltage (V)	Electrolyte	Capacitance (F/g)	References
Peanut Shells	PTFE	80:10:10	−0.2 to 0.8	1M H_2SO_4	340	**Xiao *et al.*,2018**
Activated Aloe vera	PTFE	80:15:5	-0.8 to 0.4	1M H_2SO_4	410	**Karnan *et al.*,2016**
Pinecones	PVDF	80:10:10	0 to 2	1M Na_2SO_4	137	**Bello *et al.*,2016**
Loofah Sponge	PTFE	80:10:10	0-1.6	6M KOH	309	**Su *et al.*,2018**
Sunflower stalk	PTFE	90:5:5	-1.1 to -0.2	6M KOH	365	**Wang *et al.*,2018**
Pinecone flowers	PVDF	80:10:10	−1 to 0	1M KOH	170	**Nagaraju *et al.*,2017**
Lotus leaf	PTFE	80:10:10	-1 to 0	6M KOH	379	**Qu *et al.*,2018**
Tobacco rods	PTFE	85:10:5	-1 to 0	6M KOH	286	**Zhao *et al.*,2016**
Garlic Skin	PTFE	80:10:10	0 to 1	6M KOH	427	**Zhang *et al.*,2018**
Activated Banana peel-derived porous carbon	PTFE	80:10:10	0 to 1	1M Na_2SO_4	139	**Yang & Park 2018**
Natural bamboo BC PBC1 PBC2	PVDF	80:10:10	−1.0 to 0	6M KOH	111 171	**Gong *et al.*,2017**
Activated carbon from Bamboo	PVDF	85:10:5	-1.5 to 0.5	1M KOH	498	**Shetty Ajay *et al.*,2022**
Activated carbon from Sugarcane Bagasse	PVDF	85:10:5	-1.5 to 0.5	1M KOH	486	
Activated carbon from orange peels	PVDF	85:10:5	-1.5 to 0.5	1M KOH	145	
Pueraria	PVDF	80:10:10	0 to 1	6M KOH	250	**Han *et al.*,2018**
Rubber Seed Shell	PTFE	8:1:1	− 0.2 to 0.2	1M KOH	123	**Kanjana *et al.*,2021**
Durian Shell	PTFE	8:1:1	− 0.2 to 0.2	1M KOH	178	
Palm Petiole	PTFE	8:1:1	− 0.2 to	1M KOH	177	

Active material	Binder	Ratio [AM: CM: B]	Operating Voltage (V)	Electrolyte	Capacitance (F/g)	References
			0.2			
Untreated bagasse	PTFE	8:1:1	-1 to 0	6M KOH	410	**Tan *et al.*,2021**
Pomelo peel	PTFE	90:5:5	-0.4 to 0.6	1M H_2SO_4	317	**Wang *et al.*,2019**
Bamboo fiber	PTFE	90:5:5	-0.4 to 0.6	1M H_2SO_4	286	
Sugarcane bagasse	PTFE	90:5:5	-0.4 to 0.6	1M H_2SO_4	255	
Hibiscus sabdariffa fruits	PVDF	8:1:1	0 to 2.0	0.5 M Na_2SO_4	194	**Hamouda *et al.*,2021**
Coconut shells	PVDF	75:15:5	0 to 2.0	Carboxymethyl cellulose–lithium nitrate	449	**Lee *et al.*,2021**

Allan Daraghmeh *et al.*, 2017 discussed in detail the impact of binder polyvinylidene fluoride (PVDF) concentrations (5, 10 and 20 wt.%) and pressures (~ 382 ~ 891 ~ 1783 and ~ 2547 MPa) for the fabrication of electrodes based on Carbon nanofibers (CNFs) for supercapacitors. The surface area, pore size distribution and morphology were characterized by Brunauer-Emmett-Teller (BET) method and SEM. The decrease in specific surface area was about 31 % and pore volume 14.6 % with increase in PVDF concentration from 5 to 20 wt.% at ~ 891 MPa pressure. The assembled electrodes were tested with two electrode system in aqueous electrolyte. The specific capacitance was 80 F/g for lowest concentration of PVDF (5 wt.%) and decreased about 28.3% with increase concentrations at same pressure ~ 891 MPa. In comparing the effect of pressure on specific capacitance, it increases about 38 % for (PVDF, 10 wt.%; pressure ~ 1783 MPa) from (PVDF, 10 wt.%; pressure ~ 891 MPa); their corresponding power density 24502 W/kg at energy density of 6.8 Wh/Kg and 19886 W/ kg at energy density energy of 3.8 Wh/kg.

López-Chavéz & Cuentas-Gallegos 2013 investigated the use of Nafion 5%w solution and/or Kinar Flex (PVDF) as binders at different concentrations, with DLC carbon as the active material, increased the capacitance of the electrodes from 120 F/g to 245 F/g. Binder-free electrodes assembled in symmetric 2-electrode cells showed capacitance values of 38F/g and a stable behaviour during 7000 charge-discharge cycles. Cyclic voltammetry technique was used to investigate the intrinsic capacitive nature of these electrodes.

Abbas *et al.*, 2014 studied the performance of AC/AC symmetric capacitors based on two commonly used binders-poly (vinylidene difluoride) (PVDF) and poly(tetrafluoroethylene) (PTFE)-introduced in the electrodes at same amount (10 wt%) has been compared in 1 mol L^{-1} $NaNO_3$ aqueous electrolyte. The PTFE and PVDF-based carbon electrodes exhibit capacitance values of 116 F g^{-1} and 104 F g^{-1}, respectively. Accelerated ageing performed by potentiostatic floating at 1.6 V for 120 h shows higher capacitance decrease and internal resistance increase in the case of the AC-PVDF/AC-PVDF cell due to a stronger oxidation of the positive electrode caused by the higher potential reached by this electrode.

Azam *et al.*, 2022 discussed the electrochemical properties of graphene electrodes are highly influenced by the type and amount of binder material used. Through cyclic voltammetry (CV) analyses, it was observed that as the ratio of polytetrafluoroethylene (PTFE) binder increased from 1 to 15 wt.%, the graphene electrodes exhibited the highest specific capacitance of 313.95 F/g (at 15 wt.%), followed by 135.88 F/g (at 10 wt.%), 102.75 F/g (at 5 wt.%), and 74.87 F/g (at 1 wt.%) at a scan rate of 1 mV/s. Additionally, the galvanostatic charge-discharge (GCD) method calculated a specific gravimetric capacitance of 373 F/g. The utilization of graphene and PTFE as electrode materials through the slurry technique results in electrodes with exceptional performance for supercapacitors. The study findings highlight the significance of optimizing the ratio of PTFE binder for achieving high specific capacitance and cyclic stability, thus demonstrating the promising potential of these graphene-based electrodes in advanced supercapacitor applications.

2.3.3. Effect of functional groups

The effect of functional groups on the electrochemical performance of carbon electrodes is a significant area of research due to the impact these groups have on various properties such as capacitance, ion diffusion, and stability.

Functional groups, particularly oxygen-containing ones, enhance the electrochemical properties of carbon electrodes. For example, the introduction of oxygen functional groups created electrochemical active sites and defects that facilitate ion diffusion. This results in improved electrochemical performances, including higher areal capacitance in both positive and negative electrodes **(Zhang *et al.*, 2020)**.

The presence of oxygen functional groups on the surface of walnut shell-based activated carbons positively influenced electrochemical performance metrics like specific capacitance, leakage current, equivalent series resistance, current efficiency, and stability. Acid and heat treatments applied to commercial activated carbons also lead to significant improvements in gravimetric and volumetric capacitance, demonstrating the positive effect of surface functional groups **(Wu *et al*., 2008)**.

In supercapacitor devices, synthesis and activation processes created activated carbon electrodes with high specific surface areas and tailored porosities. This engineering results in promising electrochemical performances **(Pollak *et al*., 2008)**. Moreover, the presence of CO groups at micropores on activated carbon electrodes can reduce specific capacitance by increasing the energy barrier for ion entry **(Tojo *et al*.,2014)**.

Functional groups can also influence the electrochemical oxidation behaviour of DNA on carbon electrodes, showcasing distinct oxidation signals of guanine and adenine residues **(Suprun *et al*., 2021)**. Additionally, the study of dopamine adsorption on carbon electrodes during electrochemical activation highlights the generation of graphene derivatives like graphene oxide or reduced graphene oxide, which enhance electrode performance in chemical and biological sensors **(Li *et al*., 2019)**.

Lastly, different types of carbon electrodes, such as graphite and glassy carbon electrodes, exhibit sensitivity to pH and metallic ions due to the reactions involving oxygen functional groups **(Majer *et al*., 1973)**. These functional groups can inhibit the electroactivity of molecules on carbon electrodes **(Tom and Andreas 2017)**.

The incorporation of nitrogen-containing functional groups in carbon electrodes significantly enhances their electrochemical performance, affecting properties such as electron-transfer kinetics, capacitance, and stability. Various studies highlight these improvements across different applications and material configurations. Nitrogen-containing groups in organic electrode materials serve as crucial electrochemical active sites, enhancing properties such as dissolution suppression, electronic conductivity, and redox reaction kinetics. The regulation of these molecular structures is essential for optimizing electrochemical performance **(Yu *et al*., 2021)**. For instance, nitrogen-doped

amorphous carbon thin film electrodes exhibit fast electron-transfer kinetics and altered electronic properties depending on the degree of nitrogenation **(Behan *et al.*, 2017).**

In vanadium redox flow batteries, nitrogen-containing functional groups on carbon sensed electrodes, treated with liquid ammonia, have shown improved energy efficiency, voltage efficiency, and current efficiency **(Kim *et al.*, 2014)**. Similarly, activated carbon particle electrodes modified with nitrogen groups demonstrate significantly higher desalination capacity and charge efficiency in capacitive deionization processes compared to unmodified electrodes **(Dou *et al.*, 2020)**.

Electrochemical activation of amorphous carbon nitride films imparts quasi-metallic behavior, which enhances their electrochemical reactivity **(Benlahsen *et al.*, 2005)**. The introduction of pyridinic nitrogen has been linked to increased surface area normalized specific capacitance, indicating a direct correlation between nitrogen functional groups and improved electrochemical performance **(Rennie and Hall., 2013)**.

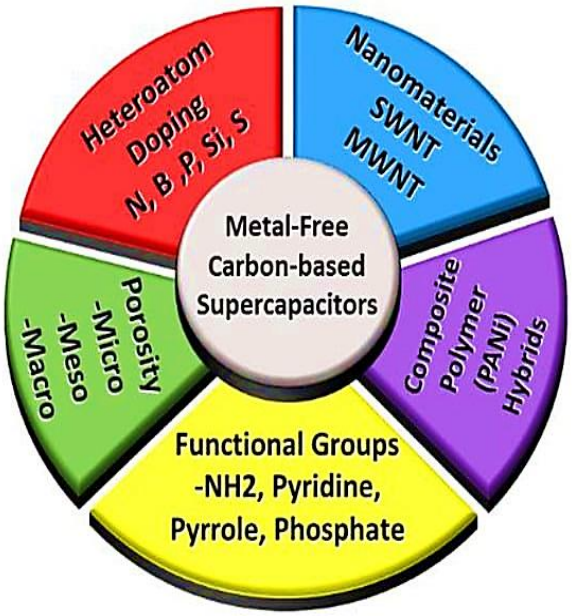

Figure 2.5: Approaches used to advance the performance of metal free carbon-based supercapacitor. (Siraj *et al.*, 2020)

Nitrogen-doped carbon synthesized from polyaniline base exhibits excellent electrocatalytic activity, particularly in the oxidation of ascorbic acid in neutral mediums **(Mutyala and Jayaraman., 2014)**. Furthermore, nitrogen functionalization in activated carbon electrodes for supercapacitors, prepared under mild conditions, leads to high

gravimetric capacitance, energy density, and enhanced durability **(Mostazo-López *et al.*, 2020)**.

The effect of nitrogen on carbon electrodes was also evident in supercapacitor applications, where nitrogen-doped carbon composites derived from metal-organic frameworks show significant enhancements in specific capacitance, rate capability, and cycling stability **(Tong *et al.*, 2017)**. The presence of quaternary nitrogen in doped configurations improved wettability, resulting in enhanced volumetric capacitance high-rate capability, and long cycle life **(Li *et al.*, 2015).**

In summary, the functional groups on carbon electrodes play a crucial role in determining their electrochemical performances. The presence of oxygen-containing groups generally enhances capacitance and stability by creating active sites and improving ion diffusion, although specific configurations of these groups can also lead to reductions in performance depending on the application whereas nitrogen-containing functional groups substantially improve the electrochemical performances of carbon electrodes by enhancing electron-transfer kinetics, specific capacitance and overall stability. These improvements are critical for various applications, including supercapacitors, redox flow batteries and capacitive deionization processes, demonstrating the versatile benefits of nitrogen doping in carbon-based materials.

2.3.4. Effect of electrolytes

The choice of electrolyte plays a crucial role in the electrochemical performance of carbon electrodes, influencing properties such as capacitance, energy density and rate capability. Different electrolytes interact with carbon electrodes in unique ways, impacting their overall efficiency and stability. Graphene-carbon composites with flat-shaped microstructures have demonstrated superior electrochemical performances across various electrolytes, making them suitable for high energy supercapacitors **(Moreno-Fernández *et al.*, 2019)**. Nitrogen-rich porous carbon materials, when used in supercapacitors, achieve high specific capacitances and energy densities, maintaining high power abilities with different electrolytes **(Yang and Zhou 2017)**.

The type of electrolyte significantly affected the capacitance values of sulphur-doped activated carbon samples. For instance, specific capacitance values were reported to be 144.7 F g^{-1} in KOH electrolyte and 101.9 Fg^{-1} in H_2SO_4 electrolyte **(Yaglikci *et al.*, 2019)**. Similarly, carbon cloth/$NiFe_2O_4$ (CC/$NiFe_2O_4$) electrodes exhibit excellent electrochemical performance in both 6 M KOH and 1 M H_2SO_4 aqueous electrolytes, with specific capacitances as high as 1135.5 F g^{-1} in H_2SO_4 and 922.6 F g^{-1} in KOH **(Yu *et al.*, 2014)**.

Functional groups on activated carbon electrodes can induce higher capacitance in organic electrolytes containing lithium salts, although they may decrease the rate capability **(Ding *et al.*, 2019)**. Additionally, the total capacitance in organic electrolyte was limited by the external surface area, whereas in aqueous electrolytes it depends on the total surface area, including micropores **(Zeller *et al.*, 2012)**.

MXene-carbon nanotube composite electrodes with knotted CNTs maximize ion accessibility, enabling exceptional rate performance at low temperatures in organic electrolytes **(Gao *et al.*, 2020)**. Poly (acrylic acid)-based hybrid inorganic-organic electrolyte membranes with titania show enhanced electrical double-layer capacitor performance, achieving a specific capacitance of 28.6 Fg^{-1} and excellent stability **(Liew *et al.*, 2016)**.

Different neutral electrolytes also impact the performance of composite textile electrodes. For example, these electrodes exhibit higher electrochemical capacitance in Ca $(NO_3)_2$ electrolyte compared to $NaNO_3$ at low scan rates, but the situation reverses at higher scan rates **(Yang *et al.*, 2016)**.

The electrolyte's composition, ion size, ionic conductivity, and interaction with the carbon electrode's microstructure critically influence the electrochemical performance of carbon electrodes. Understanding these interactions allows for the optimization of electrode materials for specific applications, ensuring maximum efficiency and durability. In summary, the intricate characteristics of the electrolyte, encompassing factors such as ion type and size, ion concentration and solvent, ion-solvent interactions, electrolyte-electrode material interactions, and the potential window, collectively shape the EDL capacitance, pseudocapacitance, energy/power densities, and cycle-life of electrochemical

supercapacitors. Understanding and optimizing these aspects are crucial for advancing the performance and functionality of ESs in various applications. In general, various types of electrolytes have been developed and reported in the literature to date. As shown in figure 2.7, these electrolytes are mainly classified as liquid electrolytes and solid/ quasi-solid-state electrolytes.

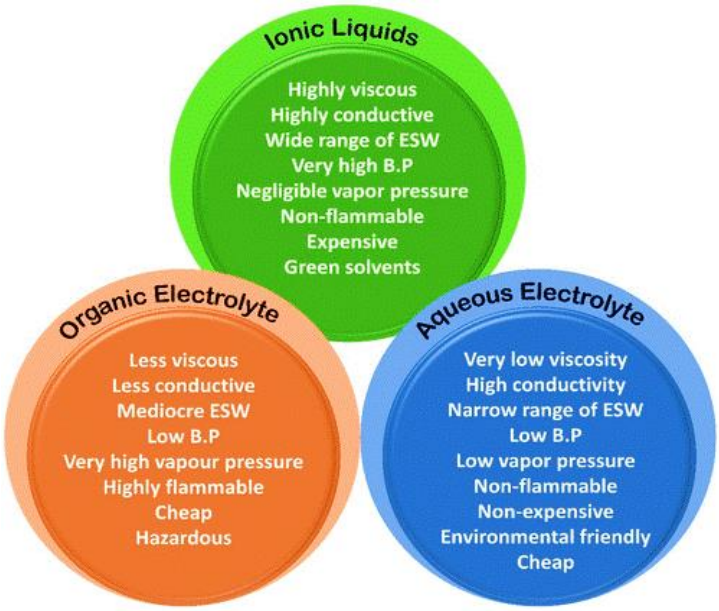

Figure 2.6: Emerging Electrolytes for Supercapacitors (Saha *et al*., 2024)

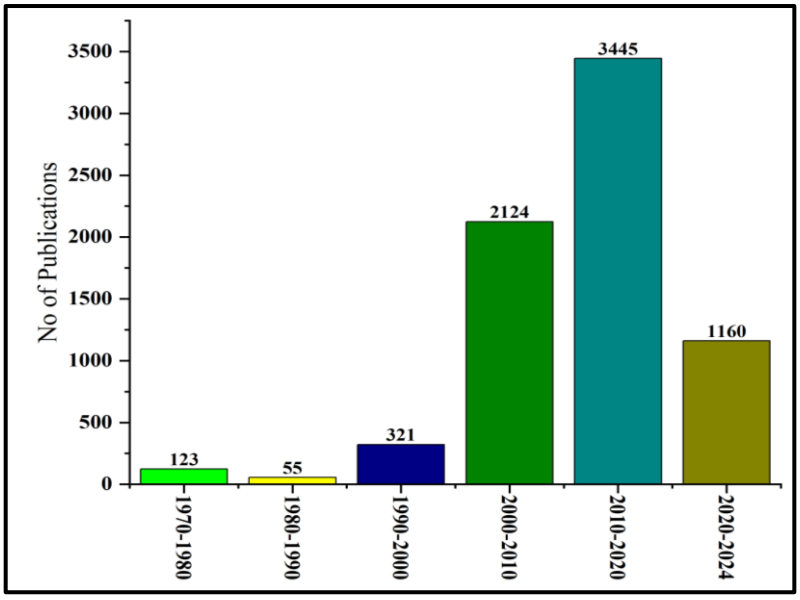

Figure 2.7: Relevant documents published pertaining to biomass carbon as supercapacitors, Source: Mendeley Data

In summary, diverse methods have been employed to prepare high-performing electrode materials from biomass-derived activated carbon materials. The extensive research presented in this chapter highlights the promising prospects of utilizing biomass wastes for electrode materials in supercapacitors. Additionally, analysis suggests that further exploration with various electrolyte classes remains open to obtaining capacitors with optimal performance.

The current research is focussed on utilisation of waste leaves of *Spathodea campulata* and *Tecoma capensis* as precursors for preparing biomass carbon and N-doped carbon for potential application as electrode materials for supercapacitors