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Capacitive Performance of Carbonaceous Electrodes for Supercapacitors-A Review

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ABSTRACT
Population explosion exhausted the fossil fuel and there is a great demand for energy and energy storage devices.Hence the industrialists and researchers hunting for alternative fuels and storage of energy system/devices. An Alternative for Better future and Carbon cutting/converting Climate-friendly(ABC) technology practiced and commercialised is only through the supercapacitors. Batteries store huge energy but charging them is a time consuming process.Capacitors can be charged immediately but store less energy. Because of the high cyclic stability and availability of electrode materials there is a possibility of improving the potentiality of capacitive performance. Designing high performance supercapacitors depend on electrode materials.Hence this paper reviews with a focus on capacitance performance of wide variety of electrode materials and carbonaceous electrodes in particular. The review aims at the capacitive performance of carbon based electrodes which influence the high performance of supercapacitors.The capacitance performance behaviour of various forms of carbon materials are analysed which are the future perspectives of the current research trend. Highlights and summary of the review emphasize the efficiency of essential electrochemical properties of various carbon based materials/composites viz., Activated carbons(AC),Porous carbons, carbon aerogels ,graphene ,lignin derived carbons , carbon nanotubes (CNT) and MXenes.Electrical double layered capacitors (EDLC) are highly efficient in storing energy due to pure electrostatic attraction between ions and the charged surface of the electrodes. EDLCs are the supercapacitors with pure carbonaceous electrode materials.Hence the capacitive characteristics such as specific surface area,porous volume/size and power density are critically reviewed and summarized with future perspectives of research.
Key Words: *Energy storage system, Supercapacitors, Carbon based electrodes, Capacitance.*

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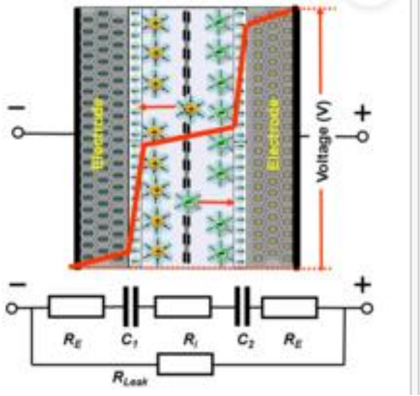
I. INTRODUCTION

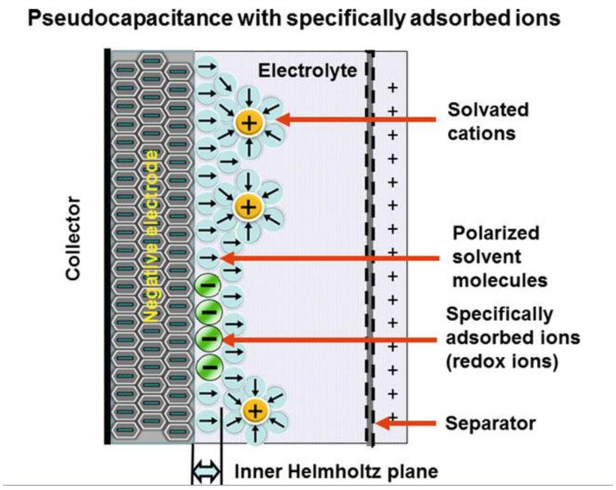
There is an increase in demand for energy due to burgeoning population.This leads to the search for alternative fuels and energy storage systems. For the past few decades energy storage systems such as lithium ion batteries and fuel cells are gaining focus because of its efficient application in industrial and domestic purposes[1,2].Performance of electrode materials and electrolytes are important in improving the efficiency of the supercapacitors. There are three types of supercapacitors such as Non-Faradaic(Electrochemical/Super capacitors), Faradaic(Pseudocapacitors) and a combination of the two(Hybrid capacitors) [3-5]. The energy storage mechanism of these types are unique and illustrated in the figures 1 and 2.

Figure-1.Charge Storage mechanism in SC



Various forms of Carbon-based materials such as powder, fiber, monoliths and foils are used in an supercapacitor device. The influential characteristics of carbon-based materials such as specific surface area, electrical conductivity, pore size and pore shape improve the high performance of supercapacitors[6-10].

Figure-2 Charge storage mechanism in pseudocapacitors



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Carbon materials such as activated carbons from various sources, graphene, aerogels,carbon nanotubes, MXenes are selected to review critically.Capacitive performance characteristics such as micro and meso porous structures, specific surface area,doped with heteroatoms, fabrication with ionic channels are discussed.

Preparation of nitrogen-containing carbonaceous materials

Nitrogen-containing carbonaceous materials can be prepared by post treatment and in situ methods.

In the in situ method various nitrogen-containing precursors are directly utilised to construct nitrogen-functionalized carbonaceous materials, including polyaniline, polypyrrole, polyacrylonitrile, melamine analogues and nitrogen-containing ionic liquids.In the post-treatment method, carbonaceous materials are treated with ammonia, urea and/or nitrogen plasma to attach nitrogen-containing functional groups [11-15].

The post-treatment method is not preferrable and it is not eco-friendly because of

i) the existence/ release of toxic gases during the processes and

ii) integration of nitrogen is limited only onto the surface of the carbonaceous materials.

Preparation of oxygen containing containing carbonaceous materials

A promising strategy to enhance the supercapacitor performance is the integration of oxygen . Mechanism of oxygen-functionalized supercapacitor electrode materials is based on the reversible oxidation/reduction of hydroquinone/quinone groups [16,17].

Oxygen containing functional groups in the graphene derivative (graphene oxide) and acid assisted functional graphene was synthesized [18,19] to enhance efficiency from 7.51% to 15.16% .

Structure / Surface characteristics of Carbonaceous materials

Carbonaceous materials can be classified as micro,meso and macroporous structures on surface of electrodes. Carbon materials possess porous microstructures, excellent mechanical performance, and high electrical conductivity are employed in the supercapacitors [20-23].Preparation of mesoporous graphene network was accessible to the ionic electrolyte and was able to operate a voltage up to 4 V. The synthesized material showed the energy density from 90 Wh.kg−1 to 136 Wh.kg−1 at 80 °C[24,25].

Carbon precursors are activated by physical and chemical agents lead the carbon based electrodes to integrate the functionalized atoms that demonstrate the charge –discharge mechanism,transport of ions,high porous structures enhancing the performance of supercapacitors.

Physical activation by high temperature or gases:

Steam leads to more meso- and macropores in the activated carbon. Carbon dioxide activation contributes to more micropores in activated carbon. Chemical activation is carbonization process by impregnate carbon precursor with certain chemicals such as H_2SO_4,KOH, H_3PO_4, $ZnCl_2$, K_2CO_3 through pyrolysis at very high temperature (700°C–1,000°C) [33-37]. Chemical activation is preferred than physical activation due to better quality consistency and shorter residence time required for activation.

Activation of carbon materials by chemical reagents

Activation of carbon materials/ carbon precursors by chemical agents promote bond cleavage, hydrolysis, dehydration, condensation and cross-linking reactions which promotes the formation of micropores. Hence the activation approach increased the heterogeneity in structure which influences the capacitance of supercapacitors(Table-1).

Table--1.Influence of Activation agents on Capacitance of Carbonaceous Electrodes

S.No	**Activation agents**	**Pyrolysis**	**Capacitance** (F/g)	**Reference**
1.	$ZnCl_2$	732°C	142.09	[33]
2.	H_3PO_4	450°C	260	[34]
3.	KOH	400°C	251.04	[35]
4.	H_2SO_4	600°C	396.5	[36]
5.	K_2CO_3	400°C	263.46	[37]

Furthermore a novel type of nanoscale sized carbon particles called carbon aerogels are synthezied organically by the polymeric condensation of resorcinol and formaldehyde through a sol–gel process with sodium carbonate as base catalyst[26-30].Another important form of carbon material is graphene.The stacking of graphene sheets (multi-layered) create nano-scaled ionic channels in the interlayers[31-33].

Lignins , the phenolic polymers which are used as carbonaceous precursor for producing high-performance carbon materials. Lignin (biomass)derived carbon electrodes attracted recent researchers to employ activated carbons (Table-2) and evident to enhance the capacitance[38-50].

Table-2- Lignin derived activated carbons and their capacitive performance

Type of Activated carbons	Capacitance F/g	Reference
Rice husk	233	[40]
Banana leaves	400	[42]
Orange peel	460	[43]
Wheat straw	222	[46]
Coconut shell	228	[48]
Cotton stalk	1964.45	[50]
Potato peel	269	[53]
Peanut shell	298	[52]
Sugarcane Bagasse	300	[54]

Future Research Focus

Research on the mechanism of the integrated heteroatoms affecting the performance of supercapacitors leads to the next level in this field.The configurations and locations of heteroatoms in the carbonaceous skeletons are not explored . Heteroatom functionalization of carbonaceous materials needs to be experimented which need further research to improve the supercapacitor performance.Furthermore the limitations of novel and advanced materials like fullerene and MXene [55]can be addressed and focused on future research.

II. Conclusion

Proliferative research on the synthesis,characterization /behaviour ,mechanism of the integrated heteroatoms ,functional atoms,potentiality of charging and discharging of ions,electrolytes,electrical conductivity influencing the performance of supercapacitors and related issues are highlighted .The summarized research focus in our review will provide a commercial potentials for the supercapacitors.

Data Availability Statement

This is a review paper and presents an overview of previously published data.

Conflicts of Interest

The authors declare no conflict of interest.

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