A Review of New Advancements in Supercapacitors High Specific Capacitance and Retention Capacity

Sakshi Kasanya, Lakshya Kumar, Preeti Ujjaineeya, Pragyesh Agrawal
Department of Physics and Electronics, IEHE, Bhopal-462016, India

Abstract: Researchers are becoming more interested in the issue of electrical energy storage as a result of the modern generation's massive and quickly growing global electrical energy consumption and requirement. Because they work so well and are useful in portable science and technology applications, supercapacitors are regarded as a possible alternative contender for electrical energy storage devices. Numerous studies are being conducted in the field of SCs to develop new and more effective electrode materials that will enable SCs to achieve high specific capacity, superior charge storage capacity, cyclic stability, and optimal conductivity. In addition to providing a brief overview of recent research on EDLC, pseudo capacitors, and hybrid supercapacitors, as well as their many varieties, principles, and applications, this brief review also summarizes several studies on different composites that are utilized as electrodes in supercapacitors

Keywords: Supercapacitors, EDLC, Pseudo capacitors, Redox Asymmetric, Specific Capacitance, Capacity Retention.

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I. INTRODUCTION

A common example of an energy storage system is a battery or a capacitor. Batteries are recommended for applications requiring long-term energy use with low power output due to their higher energy density, whereas capacitors are favored for applications requiring high power energy delivery. For fulfilling the requirements in application, the capacitors and batteries are both inadequate. As a result, novel energy storage technologies known as electrochemical capacitors, supercapacitors, or ultracapacitors are being thoroughly investigated [1]. An electrochemical device called a supercapacitor was created in the 1970s and 1980s to store energy using polarized electrolyte. Compared to the conventional chemical power source, it is different. It is a specific type of gadget that performs similarly to conventional capacitors and batteries. EDLCs and pseudo capacitors are 2 general categories of supercapacitors which are based on their mechanisms of storage. The former primarily depends upon the storage of non-faradic double-layer charge onto the electrode-electrolyte. The manufacturing of supercapacitors started in the 1980s. Supercapacitors are now being used by numerous electrical industries throughout the world for their products. The advantages and characteristics of each supercapacitor manufacturer are unique [2]. Industrialization and current development in science and technology, and the use of electronic items are all moving forward quickly [3]. Advanced electrical energy storage systems are a hot topic of research as a result of these advances [4]. The Pinnacle Research Institute of the USA created the initial supercapacitor by minimal internal resistance in 1982 for use in military relay applications. Supercapacitors are proving to be effective tools for storing electrochemical energy, which is essential for capturing renewable electrical energy and supplying the world's energy need. Recent developments in innovative functional component materials and device configurations, such as that EDLCs, pseudo capacitors (or redox capacitors) and Hybrid capacitors have effectively led to the fabrication and design of a series of supercapacitors. They have high-rate capabilities, moderate to high energy densities, high power densities, extended life, operational safety as well as electrochemical charge storage. The materials used in electrodes have a crucial contribution in determining the electrochemical characteristics, the energy storing procedure, and the mechanical characteristics of supercapacitors for storage of energy [5,6]. Capacitance and Retention Cycle are the important factors which effects the life of supercapacitor. Substances used to make the electrodes has a significant impact on the kind of capacitance a SC will encounter. Composition of materials used into the electrolyte and electrodes, capacitance varies greatly. Due to a few key circumstances, like functional groups, pore size distribution and specific surface area, materials will behave differently and that also effects the cyclability of the supercapacitors. The exploration of various composite material production techniques and their use in energy storage devices discovered till now. A variety of materials were examined, including transition metals, graphene, aerogels, conducting polymers, activated carbons made from renewable resources and Carbon Nano Tubes (CNT). Additionally, various activation strategies to boost Specific Capacitance are discussed in this review. The goal of our research is to identify the more effective materials for Supercapacitor applications by examining the Specific Capacitance and Cyclic Stability of different composites. Comparing and condensing the life cycles and capacitances of various materials [7,8].

II. PRINCIPLE OF SUPERCAPACITORS

Supercapacitor are mostly made up of numerous pieces, such as electrodes, current collectors, separators and electrolytes. The separator's job is identical to that of the battery's separator. It isolates the 2 electrodes to prevention from short circuits amid the electrodes and permits ions to pass through. The main idea behind supercapacitors are to store of electrical energy by using electric double-layer capacity created by the charge dissociation at interface amid bath solution and electrolyte. Equation (1) describing the basic idea behind SCs is based on electrostatic capacitors. The surface area (A), Relative permittivity of dielectric material (ε_r), the permittivity of air (ε_0), and the distance between two electrodes (d) are all included in this equation. The capacitance is changed by varying surface area and the thickness of dielectric material in accordance with the connection shown in equation (1)[9].

$$C=\varepsilon_0\times\varepsilon_r\times\frac{A}{d} \qquad \text{……….(1)}$$

III. TYPES OF SUPERCAPACITORS

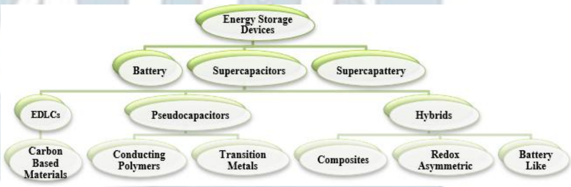


Figure 1: Types of Supercapapcitors

There are various types of supercapacitors which are depicted below:

EDLC Supercapacitors

EDLC supercapacitors are made up of two electrode materials that are carbon-based, adequate electrolytes, and a separator. With the electrochemical double-layer storage principle, EDLCs could either store charges electrostatically or through a non-Faradic way, preventing the transfer of charge loads. Carbon-based materials have shown to be the most alluring material for EDLCs. The several varieties of EDLCs include Carbon Foams, Carbon Aerogels, CDC (Carbon Derived Carbon), Activated Carbon, Graphene, and CNT (Carbon Nanotubes) [10].

Pseudo Capacitors

These faradic capacitors conduct redox processes, which causes the transference of charge amid the electrolyte and electrode. They are made utilising a variety of techniques, such as redox, intercalation, and electrospinning. Due to this faradic mechanism, pseudo-capacitors have energy densities that are higher than those of EDLCs. In this kind of capacitor, conductive polymers, metal- doped carbon and metal oxides make up the majority of the electrode materials [1].

Hybrid Supercapacitors

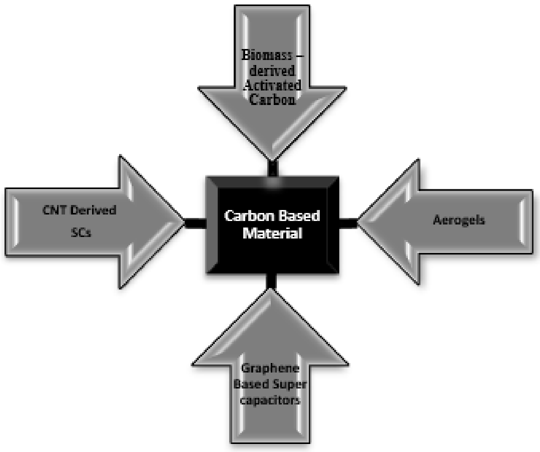
These SCs combine two electrodes with significant amounts of double-layer capacitance and pseudo capacitance. Conducting polymers and MOs (carbon-based materials) are used to create hybrid-type of SC composites [1].

IV. RECENT DEVELOPMENTS IN SUPERCAPACITORS

A supercapacitor was developed in the 1970s and 1980s in order to store energy using polarised electrolyte. It is distinct from the traditional chemical power source. It's a particular kind of device that functions similar to batteries and traditional capacitors. Based upon their techniques for charge storage, the supercapacitors could be categorised in 2 types: pseudo capacitors and EDLCs. The production of SCs began in 1979 for use in electrical vehicle starting system, which is the main source of energy for the former and the production rising in 1980s. Many electrical sectors now use supercapacitors in their products throughout many different countries. Each country's supercapacitor products have distinct benefits and qualities [10].

V. CARBON DERIVED SUPERCAPACITORS

Carbonaceous materials are the materials which are commonly used by many companies in their electronic products including supercapacitors. Carbonaceous electrode materials are highly passable as they could be synthesized in many diverse forms and can be easily found in many ways. Researchers are continuously doing research in the field of electronics to find better carbon-derived materials for electrode for making electric devices for energy storage. Already, so much research have been done which focused on carbon based materials. A most common kind of this category is activated carbons (AC)[11]. ACs are widely used by commercial manufacturers for making Supercapacitors, for their transcendence properties viz stability (thermal and chemical), cost effectiveness, high surface area, and easy availability [12]. In ACs firstly carbon goes through a physical and chemical process for making material more adsorptive and porous. Some commonly used materials are briefly describes below[11].



Biomass – Derived Activated Carbon

Sustainable biomass materials are in demand for making Supercapacitors as they are a fabulous source of nanoporous activated carbon. There are so many kinds of renewable energy sources and waste materials that are used in making Supercapacitors electrode materials with some additional chemical processes, such as Rice husks, Human hair, Willow wood, Tamarindus indica fruit shell, Cassava peel Waste, Peanut shells, Aloevera, Rotten carrots, Grapefruit peels, Coffee beans, Bacterial cellulose, Jute fibre, Paper pulp, Chicken eggshells, Tea waste, Waste coffee powder, Wild jujube pit, Poultry litter, Pomelo peels, Pinecone, Amaranths, Corncob, Tobacco rods, Fish gill, Hemp stem, Bamboo petals, Honeycomb, Shaddock peel etc. Electrodes made by these materials show amazing cycle life in SCs and their electronic devices. These all are sustainable and readily accessible in our day to day lives and due to this they are desirable materials for electrodes [13]. Summary of some researches on the utilisation of Biomass in Supercapacitors:

Table 1: some researches on the utilisation of Biomass in Supercapacitors:

Biomass	Electrolytes	S. C. (Fg^{-1})	Charge Density (Ag^{-1})	Surface Area (m^2g^{-1})	Retention Rate % (Cycles)	Energy Density ($WhKg^{-1}$)	Power Density ($WhKg^{-1}$)	Ref.
Rice Husk	KOH	80.2	1	-	90(5000)	-	-	[14]
Banana peel	KOH	173.1	0.5	-	-	-	-	[15]
Nitrogen-Doped Banana Peel	KOH	210.6	0.5	1357.6	-	-	-	[15]
Soybean-waste	KOH	220	_	-	98(10000)	-	-	[16]
Rice Husk	KOH	250	1	2523.4	-	-	-	[17]
Tea waste	KOH	256	0.5	-	95.40 (10000)	-	-	[18]
Wheat husk	KOH	271.5	0.5	-	82(5000)	-	-	[19]
Rice Husk	-	288	0.5	-	-	-	-	[20]
Jute Fibre	6M KOH	346	1	-	96(10000)	15.44	-	[21]
Acai seed	1 M KOH	346	1	-	88.30(5000)	-	-	[22]
Willow wood	6M KOH	394	1	-	94(5000)	23	10.000	[23]
Albizia flowers	KOH	406	0.5	2757.63	-	26.3	429	[24]
Human hair	NaCl	491	1	-	86(6500)	38.4	0.374	[25]

CNT Derived SCs

CNTs possess a strong mechanical strength, excellent electrical properties, good specific area and very high dimensional ratios. CNTs are far superior than the conventional Carbon derived electrode materials because of they have a large surface area to volume ratio, quick charge flowing capacity, high electrical conductivity and enormous electrolyte accessibility. CNTs can divided into 2 types: one is SWCNT and the other one is MWCNT. Surface area of both CNT's is about 5nm and they have high flexibility. Due to their inclination to get tangled to form bundles the SWCNTs are hard to handle. On the other hand, the MWCNTs having length about 20 nm, which is longer than SWCNTs comparatively and have a greater volume also, they acts like ideal fillers[1]. The production of CNTs rise up remarkably since 1990s[26]. In 1997 firstly investigated by Niu et al. that CNTs could be a good material for making supercapacitors[27]. Mechanical toughness of Carbon nanotubes (CNTs) have up to 20% of elastic strain limit, which allows them to make a very good competitor for flexible material for electrode for Supercapacitors[28]. In a study in 2018 by L. Fekri Aval, et al. fabricated three different electrode material for paper Supercapacitor from Graphite nanoparticles (GNPs), Carbon Nanotubes (CNTs) and Graphene and they found that the electrode material synthetized with CNT showed specific capacity of 411 Fg^{-1} which was higher than both the other electrode materials fabricated by GNPs and Graphene[29]. Recently Raphael D.C. Balbo et al. fabricated flexible electrode material with PDMS/ CNTs/ PANI and reported that 408 $mFcm^{-2}$/265 Fg^{-1} (at 1 mA cm^{-2}) was the optimum specific capacitance and 20 μWh cm^{-2} (25.5 $Whkg^{-1}$) was 100μ Wcm^{-2} (126.6 Wkg^{-1}) the power density of 100 μWcm^{-2} (126.6 Wkg^{-1})[30]. The composites of CuO@MnO_2 and CuO@MnO_2/N-MWCNT were synthesized in a latest study on nitrogen-doped MWCNTs by Vijay Kakani et al. In the presence of a 5 M KOH electrolyte, a specific capacity of ~ 184 Fg^{-1} at 0.5 Ag^{-1} was observed [31].

Graphene Derived Supercapacitors

Remarkable properties of graphene like mechanical, optical and electrical properties, graphene surfaced as a new electrode option to making ideal SCs. Since its discovery in 2004, various efficient synthesising methods have been developed and perfected [32]. The one atom thick sheet of graphite known as graphene is also known as a nanocomposite paper in which the atoms are arranged in a regular hexagonal pattern [33] with a surface area of 2630 m^2g^{-1}[34]. Significant advancements have occurred in some previous years in the continues rising trend in the development of graphene-derived electrodes since Stoller originally envisaged the very first graphene-based supercapacitor in 2008[32]. By using organic, ionic liquid and aquatic electrolytes, SCs made of graphene have been reported to obtain specific capacitances of 99 Fg-1, 75 Fg^{-1} and 135 Fg^{-1} respectively (at 31.9 $Whkg^{-1}$)[35,36]. A maximal specific capacity of 205 Fg^{-1} acquired by Wang Y. et al. for lowered graphene with the low agglomeration in an electrolyte solution[37]. Due to graphene's propensity to re-stack, calculating its internal capacitance is challenging. A research discovered that electric graphene's double layer had an inherent capacitance of 21Fcm^{-1}. As opposed to that, the interfacial capacitance can be studied on the surface area and the number of layers present[11]. These properties endow the ability to enfold densely while still having a major particular surface area to the interaction of ions and electrons[35]. It has too high mobilities which can attain 200,000 $cm^2V^{-1}s^{-1}$ at the room temperature, what allows for quick transport of ions and electrons over the various device interfaces (electrode/collector and electrode/electrolyte). It exhibits good electrical conductivity. Additionally, due to its higher electric conductivity, graphene could serve the highly active component as well as current collector, eliminating the necessity for other components as additives and binders[38]. Graphene reported bidirectional strain of unto 25%, graphene also demonstrates exceptional mechanical strength with a Young's modulus about 1TPa[39]. Because of its high capacitance retention, it is appropriate for use in printable and flexible electronics [32].

Many studies and research projects have been conducted on graphene and graphene-derived composites for use in SCs all around the world. Some of these includes conducting polymer (like polyaniline, polythiophene and polypyrrole), metal nitrides (like VN and Ni_3N), sulphides (such as FeS_2 and MoS_2), MXenes, and graphene hydroxides (such as MnNi-LDH)[11]. These graphene composites played significant roles in the electrode materials and electrical uses of SCs. Summary of some researches on the utilisation of Graphene in Supercapacitors:

Table 1: Summary of some researches on the utilisation of Graphene in Supercapacitors:

Graphene Composites	Electrolytes	S.C. (Fg^{-1})	Charge Density (Ag^{-1})	Capacity Retention	No. of Cycles	Specific Power Density (Wkg^{-1})	Specific Energy Density ($WhKg^{-1}$)	Ref.
RGO	KOH, aqueous H_2SO_4	260	-	-	-	-	-	[40]
GO@MIL-101	3 M H_2SO_4	302.47	1	80.01	9000	-	-	[41]
NG/Fe_3O_4	-	386	-	-	-	-	-	[42]
ZnCo-MOF/GS	-	695	1	78	7500	5037	108	[43]
GO:PCHRYS	-	715.3	0.5	-	1000	-	-	[44]
EG-PANI	$(NH_4)_2SO_4$	736	0.2	-	-	-	-	[45]
GO/PANI/$CuCo_2O_4$	-	741.39	1	-	-	5997.61	62.54	[46]
Ni/Co-MOF-Rgo	-	860	1	91.6	6000	42.5 kW kg^{-1}	72.8	[47]
HOrGO/TMOs	-	910	-	89.9	2000	-	-	[48]
GO@PPy-1	-	1532	-	41	1000	500 µW cm^{-2}	114 µWh cm^{-2}	[49]
Ni/G	-	1900	-	72	10000	5 $kWkg^{-1}$	37	[50]
Gd_2O_3/Co_3O4/rGO/NF	-	3616	-	-	-	-	-	[51]
$CoWO_4$-$CoMn_2O_4$/N-doped graphene (CCNG)	-	4133.3	2	96.96	5000	2250	116.25	[52]

Aerogels

Carbon Aerogels are extremely lightweight synthetic materials that are made from organic gas gel. The notable physicochemical characteristics of carbon aerogels, which are three dimensional hierarchical multiple scale porous substances, posesses higher specific surface area, lower density, higher porosity, great electrical conductivity, very good heat resistance, hydrophobicity, strong chemical stability and adaptable surface chemistry. The majority of activated carbons are less conductive than aerogel electrodes [33]. Aerogels were first invented in 1932[53]. Due to their extremely low density, abundant porosity and multifunctionality aerogels show a wide range of applications [54], like dampening elements [53], environmental safeguards, sensors, catalysts, energy storage, insulation materials, electro-magnetic metamaterials, filters, sorbents and flame retardants. Carbon, Silica, organic metal–oxide, metal-organic aerogels and inorganic-organic hybrids are different types of aerogels which have been synthesized through various preparation and precursor methods[55]. Numerous number of aerogel composites are developed by researchers for making electrodes for SCs of an ultra-long life cycle and great capacitance with less retention. Recently Ming Zhang at el. fabricated Aerogel composites and found exciting results at different combinations. The positive charge electrode material made by MCNF@H-Co_3O_4 aerogel and the negative charge electrode material prepared by NO-HMCNF aerogel shows the specific capacity of 1600.6 Fg^{-1} at 1 Ag^{-1} and 362.5 Fg^{-1} at 0.3 Ag^{-1}, retention rate of 90.5% (30,000 cycles at 20Ag^{-1}) and retention rate of 95.5% (30,000 cycles at 5Ag^{-1}) respectively. With a retention rate of 90.1% after 5000 cycles (at 5Ag^{-1}), the supercapacitor made with MCNF@H-Co3O4/NO-HMCNF exhibits a remarkable energy density of 51.9 $Whkg^{-1}$ at 750.3 Wkg^{-1}[56].

VI. CONDUCTING POLYMERS

Large molecules with a structure made up of several repeating units are referred to be polymers. Numerous tiny molecules, known as monomers, are the building blocks of polymers, which are formed into large chains via covalent connections. Jons Jacob Berzelius came up with this word in 1833[57]. Among polymeric materials, conducting polymers are regarded as the fourth-generation materials [58]. The conducting polymers were discovered in the late 1970s[59]. Polyacetylene was the first synthetic polymer to exhibit substantial conductivity. Conductive electroactive polymers have become the focus of technological development ever since the discovery of conductive polyacetylene. Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa honored with the Nobel prize in 2000 for their work on "invention and development of conductive polymers". For the first time, they effectively synthesized polyacetylene as a silvery film by acetylene applying the Ziegler-Natta catalyst in 1974[60]. The desire for more sophistication, accuracy, durability, processability, and cost-effectiveness from modern technology and the structuring of performing polymer research in line with the aforementioned demand are the 2 main factors behind this research's unceasing growth. Conjugated double bonds along the length of a conducting polymer's backbone are a crucial and distinctive characteristic [58,60].

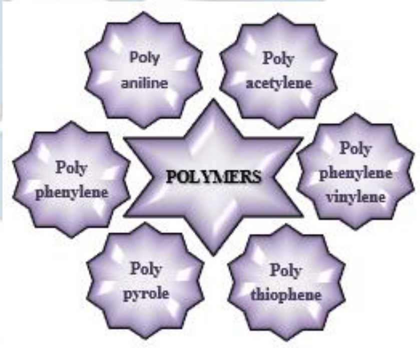


Figure 2: Types of Polymers

The single and double bonds, are brought about by the highly delocalized, polarised and electron dense p-bonds. There are some polymers with high conductivity include PANI, PA, PTH, PPV, PPy and PF. Various methods are applied to create conducting polymers, including electrochemical polymerization, chemical oxidation, hydrothermal, electrospinning, vapour phase synthesis, photochemical methods, self-assembly, the solid-state method, inclusion method and plasma polymerization [61]. CPs and their composites have various applications; industries are using them in Lithium-Ion Batteries, Solar Cells, Fuel Cells, Light Emitting Diode (LEDs), Supercapacitors, Actuators, Sensors (Gas Sensors, Bio Sensors, Chemi resistor Sensors, Strain Sensors), Corrosion protecting agents, used as electrocatalysts and photocatalysts in Biosensors, Cells, and Energy-related devices, Electronics, Shape Memory Polymers, Optical Limiting, Biomedical (Tissue Engineering, Diabetic Monitoring, Drug Delivery) etc[62]. In the realm of research, attention is not just concentrated on CPs with dopants, but also on the manufacturing of composites utilising materials like metal oxides and activated carbon. At a current density of 1Ag^{-1}, Shahbaz Khan et al. explored electrods for supercapacitors using PANI:PPy/AC and PANI:3,4- PEDOT/AC. The specific capacitance of PANI:PPy/AC and PANI: PEDOT/AC were reported at 611 Fg^{-1} and 586 Fg^{-1}, respectively. PANI: PEDOT/AC and PANI:PPy/AC were found to have assessed power densities of 2160 Wkg^{-1} and 44 $Whkg^{-1}$ respectively, and corresponding composite energy densities of 2094 Wkg^{-1} and 40 $Whkg^{-1}$ at retention rates of 90% and 92%[63]. Synthesis, Electrical Conductivity Characterization and Measurements of Polypyrrole/Montmorillonite Nanocomposites have been reported by Parmar P. et al. in 2012[64]. Investigation of the Electrical, Mechanical and Structural actions of PPY/PVA/SWCNT Ternary Composites has been published by Agrawal P. et al. in 2013[65]. On the other hand, Agrawal P. et al. have also reported Electrical, Mechanical and Structural Characterization of Polypyrrole /Poly (methyl methacrylate)/Fly ash Composite in 2013[66].

Table 2: Summary of some researches on the utilisation of Polymer in Supercapacitors:

Polymer	Composites	Electrolyte	S.C. (Fg^{-1})	Charge Density (Ag^{-1})	Capacity Retention	No. of Cycles	Energy Density ($Whkg^{-1}$)	Power Density (Wkg^{-1})	Ref.
PPy	PPy/ZnO	1 M KCl	100.17	0.5	70.71	5000	4.62	5980	[67]
	PPy/paper	polyvinyl alcohol/H_3PO_4	247.4	-	-	-	-	-	[68]
	PEDOT:PSS/PPy	0.5M HCl	393.8	50 A c m^{-3}	52.8	-	8.3	389.1	[69]
	(PPy@MXene)@Cotton	1 M H_2SO_4	506.6	1	-	-	-	-	[70]
	PPy-N	PVA/H_2SO_4/EG	509.8	0.5	100	1000	-	-	[71]
	PPy/rGO|Ni–Co LDHs	2 M NaOH	1018	1	89	5000	46.5	464.9	[72]
	$CeVO_4$/Ppy	1 M KOH	1236	0.75	92.60	10,000	52.2	675.9	[73]
PDMS	AuNWs/PDMS	-	8.5	-	-	80	25.5	126.6	[74]
	SWNT/PDMS	-	22.2	-	94	500	-	-	[75]
	MCNT/PDMS	-	90.42	-	-	20	-	-	[76]
	PI/PDMS	-	134.61	-	-	-	-	-	[77]

	ACNTA-PANI/PDMS	-	265	-	76	5000	20 μW h cm^{-2}	100 μW cm^{-2}	[78]
	TEG/PDMS	-	287	-	-	-	18.0 $kWhKg^{-1}$	21.1	[79]
PANI	YC/PANI	1M H_2SO_4	500	1	95.40	5000	16.9	550	[80]
	rGO/ Fe_3O_4/PANI	-	610	1	87	1000	-	-	[81]
	PANI-NiO	1M H_2SO_4	623	1	89.40	5000	-	-	[82]
	Cus/PANI/ MoS_2(CSPM)	-	759.2	0.25	92.10	6000	39.1	659.9	[83]
	rGO/PANI	-	853.7	1	92.60	8000	14.8	6.7 kW kg^{-1}	[84]
	PANI/SnS_2 @CNTs/CFs	-	891	2	83.80	6000	38.7	1 $kWkg^{-1}$	[85]
	HCNFs/PANI	-	1196.7	5	90.10	3000	60.28	1000	[86]
	$As_3Mo_8V_4$/PANi/Rgo	-	2351	1	96.90	5000	88.1	349.6	[87]
	PANI-Co_3O_4	-	3105	-	74.81	3000	58.84	0.16 kW kg^{-1}	[88]
PTH	PTHA//charcoal	PVA/KOH gel	265.14	2	94.61	2000	42.0	735.86	[89]
	GO-TB	2 M KOH	296	0.3	91.86	4000	148	41.6	[90]
	PD_2ET-g-SWCNTs	-	399	1	91	8000	22.5	500	[91]
	polythiophene/Al_2O_3 (PTCA)	KOH	780.4	0.5	90.54	5000	58.04	533.02	[92]
	rGO/Ag/PTh	1 M H_2SO_4	953.13	-	91.88	1000	28.8	2843.3	[93]

	GNPLs/PTh	-	960.71	0.25	84.90	1500	2.25	23.55	[94]
	PD4ET-g-GO	1.0 M H_2SO_4	971	1	98	10000	66.11	350	[95]
PF	PTFu		392	5	67	500	-	-	[96]
PA	PA-100–KOH	KOH	241	0.1	91.70	2000	-	-	[97]

VII. TRANSITION METALS

Metal oxide materials have attracted scientific attention and have been used for applications in making devices for storing electrical energy because of their distinctive chemical and physical features[98]. There has been a lot of research done on metal oxide (MO) RuO_2. Despite having a low ESR this metal oxide has a very high specific capacitance. However, in a view of that it is more expensive than other transition metal oxides, research has diversified to look at alternative options[1]. There are multiple kind of Metal Oxides, Metal Hydroxides and Layer Double Hydroxides which are studied for making energy storage devices like Super capacitors[99], Some are RuO_2[100], ZnO[101], MnO_2[102,103], TiO_2, NiO_2[104], V_2O_5[105], Co_3O_4[106], IrO_2[107], Nb_2O_5[108], Fe_3O_4[109], $Ni(OH)_2$[110], $Co(OH)_2$[111], NiAl-LDH[112], Mesoporous ternary oxides XCo_2O_4[113,114,115], quaternary mixed oxides ($CuNiCo_2O_4$, $CuMnCo_2O_4$, $MnNiCo_2O_4$) [116], $AMoO_4$[117,118,119]. Bimetallic oxide materials are more sought than single metal oxides because they may overbear the limitation of single metal oxide material's weak electric conductivity, achieve a high capacitance and at this power-level of the capacitor, enhance the energy density[120]. A study on the specific capacity of RuO_2/graphene-based electrode materials for Supercapacitors reveals that they had a specific capacity of 1561 Fg^{-1} at a power density of 21 $kWkg^{-1}$. The study also found that the energy density of RuO_2/Cu/Gr electrodes was excellent, coming in at 13 $Whkg^{-1}$. RuO_2/Cu/Gr electrode demonstrated a very excellent energy density of 13 $Whkg^{-1}$ at a power density of 21 kW kg^{-1} and displayed a specific capacity of 1561 Fg^{-1} at that level of power. [121]. In a study done by Shengyu Zhou in 2020 NiO film displayed specific capacity at 1 $mAcm^{-2}$ of 2.08 Fcm^{-2}[122]. Recently ZnO nanorods/MnO2 derived 1.6V hydbrid supercapacitor was studied by Kamran Khan et al[123]. Nanocomposite based on TiO_2/CuSe studied by Muhammad Zia Ullah Shah et al. recently[124]. Studies trending on the composites of transition nowadays which are showing very interesting results. In 2018 a Study done on $ZnCo_2O_4$@NiO by Ting-Feng Yi et al. displayed the fabulous specific capacitance of 2797 Fg^{-1} (current density 1 Ag^{-1}), and 2287.2 Fg^{-1} (at 10 Ag^{-1}). At 40 A g^{-1} the material's specific capacitance calculated by team was 1079.2 Fg^{-1} which was also amazing[125]. NiC_2O_4@NiO was used to construct an electrode material in 2017 by Dong He et al. The research revealed an intriguing specific capacity of 2287.09 F g^{-1} (at 1 Ag^{-1}) and 95% cycle stability remanent across 10,000 cycles[126]. With the use of three electrodes, Xuan HC et al. were able to achieve a greater specific capacitance of 3380.3 Fg^{-1} (1 Ag^{-1}) and observed a retention rate of 81.1% after 6000 cycles. [127].

Some Principal Elements:

$$C_t^s = \frac{n \times F}{M \times V} \quad \text{………} \quad (2)$$

C = Metal oxide's Theoretical specific capacitance

n = Number of electrons

F = Faraday's Constant

M = Molar Mass of MOs

V = Operating voltage window

$$E = \frac{CV^2}{2} \quad \text{.........} \quad (3)$$

E = Energy Density

$$P = \frac{V^2}{4R} \quad \text{........} \quad (4)$$

Table 3: Summary of some researches on the utilization of Transition Metals in Supercapacitors:

Transition Metals composites	S.C. (Fg^{-1})	Current Density (Ag^{-1})	Capacity Retention (%)	No. of Cycles	Energy Density ($Whkg^{-1}$)	Power Density (Wkg^{-1})	Ref.
RuO_2/PANI	40.2	-	-	-	-	-	[128]
Co_3O_4MBs	282.3	1	74.6	4000	-	-	[129]
rGO/RuO_2	347.28	-	-	-	-	-	[128]
rGO/RuO_2/PANI	723.09	-	-	-	-	-	[128]
$CuCo_2O_4$/CuO@RuO_2	862.5	-	90.1	8000	-	-	[130]
NiCoMn–S-h	948	1	-	-	44.9	780	[131]
V_2O_5@RuO_2	971	-	80.4	10000	174.2	450	[132]
Ni/Co-MOF	1067	1	68.4	2500	-	-	[133]
MoS_2–NiO	1080.6	1	101.9	9000	-	-	[134]
($CoFe_2O_4$/Mxene	1268.75	-	97	5000	-	-	[135]
(Ni-Fe)-P-C@HCNFs	1392	1	89	10000	-	-	[136]
Ni–Co–S/G	1492	1	-	-	43.3	0.8 kW kg^{-1}	[137]
Carbon@Co_3S_4/Ni_3S_2/NF	1716	-	90	5000	11.15 mWh cm^{-3}	600 mW cm^{-3}	[138]

VIII. COMPOSITES

The researchers continuously trying to find more powerful and efficient materials for electrode of Supercapacitors, many are working towards composites to find the new ways for more capable electrode materials. Sacchidanand S. Scindia et al. studied on composite based on Conducting Polymer and Metal (Nickel and ferrite/polypyrrole) based composite for Supercapacitor electrode material with the help of situ chemical oxidation process. The effect upon stability and specific capacitance of electrode with the concentration of electrolyte were studied. They were recorded the maximal specific capacitance by the electrode (NFO/Ppy) was 721.66 Fg^{-1} and they also determined specific energy, coulomb efficiency and specific power, of 51.95 $Whkg^{-1}$, 99.08% and 6.18 $kWkg^{-1}$ respectively[139]. The electrochemical behaviour, synergistic effects of GO content to Co-BTC were investigated by Tianen Chen et al. with very good rate capability, the greatest specific capacity measured (1 Ag^{-1}) was 1144 Fg^{-1}. 88.1% exceptional life stability has been maintained by $CoBTC@GO_2$ after 2000 cycles[140]. Anthony P. Leggiero et al. research on Cu/CNT hybrid, Cu-CNT made conductors generated through just the electrodeposition have specific conductivity values that are 3-5 times lower than those produced by Cu loaded conductors ranging from 30 to 95 percent by weight. These conductors employed electrodeposition in conjunction with CVD Cu seeding. Cu/CNT hybrid conductor obtained 28.1 MSm^{-1} electrical conductivity and 5632 Sm^2kg^{-1} specific conductivity[141]. The usage of nanocomposites in the creation of energy storage devices is becoming increasingly popular due to its affordability and environmental friendliness. Recently Date fruits were used in a simple hydrothermal method to create biocarbon-based MoS_2 (Bio-C/MoS_2) nanoparticles. At 0.5 Ag^{-1} Bio-C/MoS_2 based material exhibits the specific capacity of 945 Fg^{-1} and after 10000 (charge/discharge) cycles material showed an excellent stability of 92%. Power density and Energy density are 3800-8000 Wkg^{-1} & 74.9–157 Wh kg^{-1} also recorded respectively by Hansa Mahajan et al[142].

IX. ASYMMETRIC SUPERCAPACITORS

Asymmetric Supercapacitors

Asymmetric Super capacitors are built with two different kind of electrode material and have the particular advantage of having a vast operational voltage window, which greatly improves energy density [143]. The two electrodes of asymmetric SCs rely on redox faradic reactions as well as non-Faradic reactions and electric double-layer (non-Faradic/electrostatic) desorption or absorption [144]. For the purpose of achieving high energy density, superior cycle stability and great specific capacitance numerous studies are continuously in progress since many years. Liu Qun et al. studied $Co_9S_8@NiCo_2O_4$ for nano brushes for flexible Asymmetric Supercapacitors and they discovered outstanding findings on the specific capacity of 1966 Fg^{-1} (at 1 Ag^{-1}) and after 5000 cycles the retention rate of 92.9% was recorded. The synthesized material proven that $Co_9S_8@NiCo_2O_4$ results were more efficient than single $NiCo_2O_4$ and Co_9S_8[145]. In 2019 carbonized iron-polyaniline and vanadium dioxide-based electrode material synthesized by N. M. Ndiaye et al. and at the energy density of 1 Ag^{-1} the research showed the specific capacity of 47 $mAhg^{-1}$[146]. Deyang Yu et al. Fabricated $ZnCo_2O_4@MnO_2$ based Asymmetric SC and the specific capacity of 2170 Fg^{-1} (2.60 Fcm^{-2}) was recorded, which shows that it is a strong contendor for SCs [147]. Adeel Akram et al. recently prepared electrode for Supercapacitor (Asymmetric) derived by Graphene and MOFs nanoplatelets for high performance Supercapacitor and they used MOFs/GNPs and GNPs and reported the maximal specific capacity of 7500 Wkg^{-1} and 7370 Wkg^{-1} (at 1 Ag^{-1}), power densities of 85.8 $Whkg^{-1}$ and 60.7 $Whkg^{-1}$ at 97.7% and 97.1% respectively [148].

X. BATTERY LIKE

Earlier this decade, a range of electrode materials have been synthesized. Pseudocapacitive and battery-like materials are now in vogue for this purpose [149]. Supercapacitors that replicate batteries have excellent characteristics [150]. Battery-Type electrode materials in comparison with EDLCs offers a definite advantage as they can often provide higher energy density. Additionally, these materials can store a lot of charge storage and may conduct bidirectional processes of electro-chemical reactions took place relatively quickly.[149]. With the use of graphene foam and zinc oxide, Sibel Kasap et al. created the electrode material for a battery-like supercapacitor in 2019, and the synthesized material's specific capacity was obtained to be 448 Fg^{-1}[151]. Recently Graphitic Carbon Nitride Nanosheets and Nickel–Cobalt Oxalate used by Sourav Ghosh et al. for the fabrication of electrode of battery-like Supercapacitor. Their produced material ($NiCo_2C_2O_4/g\text{-}C_3N_4$) has a specific capacity of 1263 Fg^{-1} (at 1 Ag^{-1}) and a specified energy of 35.54 $Whkg^{-1}$ (at a specific power of 226.36 Wkg^{-1})[152]. When working with $Ni(OH)_2$/RGO, Yusuf Khan et al. that the material's maximum specific capacity was 513.8 Cg^{-1} (at 10 mVs^{-1}) and that its energy density was 119.4 $Whkg^{-1}$ (at 1250 Wkg^{-1})[153].

XI. APPLICATIONS

The erection of suitable energy storage systems is necessary in light of the growing pressures to attain carbon neutrality and expand renewable energy sources [154,33]. Nowadays Supercapacitors and also Micro supercapacitors, for instance token gold caps are frequently utilized as power sources for IC memory and microcomputers which are maintenance free. There are so many applications of Supercapacitors in different types of fields like, Transport Industries (hybrid electric cars, electric bikes, hybrid trucks), Starters, SAM (Super Accumulator Module), UPS (Uninterruptable Power Supplies), Voltage repartition, GSM, Toy making, Telecommunication [155]. Supercapacitors are widely used in Power generation plants (solar panel positioning, wind mill pitch control), Medical applications (like heart pacemaker), Satellites, Telecommunications, Electric propulsion Flight control as well. In space (Synthetic Aperture Radar (SAR), Geostationary Orbit subsystems, Mars exploration mission, Supercapacitor banks and Li-Ion batteries combined in a hybrid system, Power Bus voltage regulation, Electric propulsion, Electrical thrust vector control for launchers, Earth-observing missions using smaller satellites with high-power radar)[156] are some another transcendent usage of Supercapacitors. For more instance in Microsupercapacitors Integrated system like Microsupercapacitors Integrated with Sensors (Gas Sensors, Photodetectors, Sweat Sensors, Temperature sensors, tactile Sensors)[157], Multifunctional Microsupercapacitors (Foldable MSCs, Stretchable MSCs, Self healing MSCs, Waterproofing MSCs and Transparent MSCs), Self Power energy generated systems (Wireless Charging Generators, Solar cells, and Piezoelectric Energy Generator or Turboelectric Energy Generator), All in one devices (Wireless Charging MSCs, Photoswitchable MSCs, All in One Sensing Patch and Self Charging Electrokinetic Supercapacitors, Thermosettable MSCs) on and on[158].

XII. CONCLUSIONS

As world's population continuously hike day after day the scarcity of energy resources and growing energy crisis, needs assistance of eco-friendly, efficient, easily available, less expensive, less noxious, easy to use and liquidate energy storing devices. Supercapacitors are a good example of promising candidates which could be a helping hand us to get out of this trouble. In this review we discussed about, the timeline of their development, their working principle, working process, fabrication method, brief summary and numerous applications of various kinds of supercapacitors and their electrode materials. There are so many studies are done in this field and many more will be supposed to. As supercapacitors have a lot of applications in different electronic devices and the devices used in many fields like military applications, Transportation, Telecommunications, Space Sciences, Medical applications, Satellites and many more. This study highlighted some of the latest trending researches in the field of making supercapacitors and their electrode materials. The new innovative creations in this field would be done to finding less expensive, easily available, time saving and great conducting materials. Biomass derived activated carbon, Conducting Polymers and their composites would be the great substitutes as they are an excellent example of sustainable, easy to prepare, organic and light weighted materials and they perform very well in supercapacitors application. Rapid use of electrical energy in military gadgets, space station, high-definition security cameras, tracking sensors and for Cyber security purpose the supercapacitors may use for mankind.

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