

Hybrid Supercapacitor Application for Future E-mobility

Manish Mishra¹, Amit Pal^{2*}, Amrisha K. Panwar³

Abstract

With the rise in demand for automobiles, there is an increase in pollution levels and global warming since the past decade, there is a strong need for an alternative mode of commuting like Electric vehicles against conventional gasoline/diesel-powered vehicles to safeguard the planet and its flora and fauna. Battery technology like lithium-ion and others has already revolutionized the automotive world, but there is a limitation of fast charging, operating temperature range, and low cycle life due to degradation in the battery because of chemical reactions associated with each charge and discharge cycle. This aging or degradation minimizes operating life, slow charge/discharge process due to electrochemical reactions involved, low safety rating, usage of rare earth elements like cobalt, nickel, and lithium, etc. contributed to the extraordinary cost of LIBs system. These factors are major challenges that are hindering electric vehicle acceptance widely. Against other energy storage devices, supercapacitors and BSHs can be the potential alternatives in the domain of energy storage systems for future mobility which can address all the battery concerns. However, low specific energy is the prime concern that is required to optimize to maximize the higher range of EVs. This paper deals with types of supercapacitors and battery-type super hybrid capacitors (BSHs), it's working, along with factors influencing specific energy of supercapacitor/BSHs by improving specific capacitance and their operating voltage, also the adoption of alternate biodegradable, abundant materials for bringing down the cost of BSHs. The main goal of the study is to present BSHs as the best alternative for future mobility, having the best of LIBs and supercapacitor benefits, also brief information about the scope for the usage of alternate materials for electrodes and electrolytes for offsetting the higher cost of raw materials like lithium, graphene, etc.

Keywords: Specific energy, specific capacitance, operating voltage, BSHs, LIBs

INTRODUCTION

Due to the increase in fuel costs and concerns related to the environment, battery-operated electric vehicles (BEVs) and hybrid vehicles (HEVs) can be the best alternative mode of commuting. Currently, lithium-ion batteries (LIBs) and supercapacitors [1, 2] are the only energy-storing devices that are in mass production available. Due to the highest energy density [3, 4] of LIBs, it is preferred

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most for electric vehicles (EVs) with the highest claim range of over 500 km. However, there is a drawback of a long charging time of several hours in LIBs and other available batteries which limits EV adoption widely. Therefore, it is required to have higher specific energy which can comply with the demands of real-world driving conditions of EVs like, quick charge and discharge, higher energy density, i.e., longer range, higher power density, safety, high cycle life, a broad range of operating temperature, etc. A supercapacitor is the best solution to form a bridge between the existing capacitor and battery and thus meet the aforementioned EVs requirements. The supercapacitor has the potential of flash charging

from a fraction of a second to minutes [5], and its overall charge-discharge of approx. 10,00,000 cycles with very less degradation in performance. The only issue with a standard supercapacitor is its low specific energy of range 10–20 Wh/kg [3] which has limited its application where enormous power density and discharge at lighting-fast speed is required like airbag operation in automobile and cabin door switchers for airplanes. Supercapacitor's longer cycle life is the prime factor to consider over LIBs (Table 1), which is much beyond the cycle life of LIBs (Table 1) for instance, approx. 2000 times, or 4–6 years in case EVs are getting charged daily once. Whereas supercapacitor life is beyond 15 years. It is due to the phenomenon of storing electric charges. Electrostatic charges reside on the surface of the electrode, whereas LIBs store them in the form of chemical reactions. Furthermore, supercapacitors have fast charging of some seconds to minutes, comparatively much less than the fuel required to fill in conventional IC engines powered vehicles. A major challenge is its range (specific energy) in km. For its adoption in EVs minimum of 100 km, it should deliver. (Ensuring charging provisions similar to currently available fuel filling stations). Thus, the required energy density must be greater than 100 Wh/kg. As below comparison is self-explanatory, about the energy density area where research and development of supercapacitors are to be carried on making its performance competitive with LIBs. In this paper, the relevance between energy density, capacitance, and working voltage is summarized in Table 1. Various components such as the anodes, cathodes, pore size, surface area, and high voltage electrolytes have drawn attention for conducting research to have improved performance and lowering its manufacturing cost.

Table 1. Comparison of performance parameters between supercapacitor, battery, and hybrid supercapacitor [6, 7].

Supercapacitor vs. Battery vs. Hybrid Supercapacitor			
Parameter	Supercapacitor	Battery (Lithium-ion)	Hybrid Supercapacitor
Power density (kW/kg)	~10	1	5
Energy density (Wh/kg)	~10	450	~222, 383.2
Charge/discharge Cycle	100 k	500–1000	100 k
Cycle life(years)	15+years	4–6 years	10–15 years
Operating temperature range	–40°C to +100°C	–20°C to +60°C	–25°C to +85°C
Principle	Electrostatic	Electrochemical	Electrostatic+Electrochemical
Charge time	~10 to 15 secs	~30 to 120 mint	~5 to 10 mint
Max. rated voltage (V)	2.3 to 2.7 V	4.1 to 4.3	3.8
Min. operating voltage (V)	0	2.5	2.2
Safety	Highly stable	Safety consideration required	Highly stable
Self-discharge	Susceptible	Very low	Very low
Internal resistance	Low	High	Medium

SUPERCAPACITORS

According to energy storage methods, the supercapacitor is categorized into three types. Figure 1 illustrates classification based on electrode materials [8, 9].

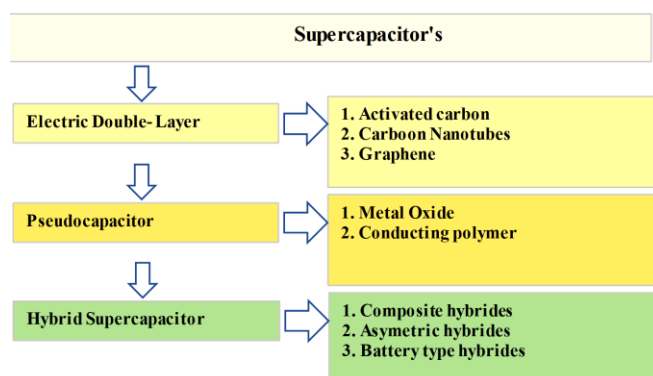


Figure 1. Classification of supercapacitors.

Electrochemical Double-layer Capacitor

Liquid electrolytes like KOH, H₂SO₄, etc. are being used between electrodes. Helmholtz double-layer built up on electrode-electrolyte conductive interface results in fast adsorption and desorption of electrolyte ions, this adds to the higher power density of the supercapacitor through a non-faradaic process. Electrode dimension, its effective surface area, and the thickness of the Helmholtz layer have a significant influence on the capacitance of the electrochemical double-layer capacitor (EDLC). Carbon electrode with porosity has energy densities around 10 Wh/kg, as their specific capacitance is (lower than 200 F/g), and their working potential is lower than 1.0 V. As every electrode-electrolyte interface can be referred to as a capacitor hence EDLC can be treated as two capacitors connected in series [9]. The Schematic of a Basic EDLC Supercapacitor is depicted in Figure 2. Its equivalent capacitance will be the addition of two electrodes. Every interface capacitance (C_{dl}) will be equal to $C_{dl} = A\epsilon/4\pi t$, where A is the effective surface area, ϵ is the dielectric constant, and t is double-layer thickness. For supercapacitor, specific energy (E) and power density (P) are derived by $E = 1/2 CV^2$, $P = V^2/4R$; where C is capacitance, V is voltage, and resistance is denoted by R [10]. As per the equation, Improvement in capacitance and working voltage requires much research work for increasing the specific energy of supercapacitor, the relevant factors are mentioned in Figure 3. Carbon materials with high porosity are preferred like activated carbon (AC), carbon nanotube, and graphene for electrodes to enhance their specific energy.

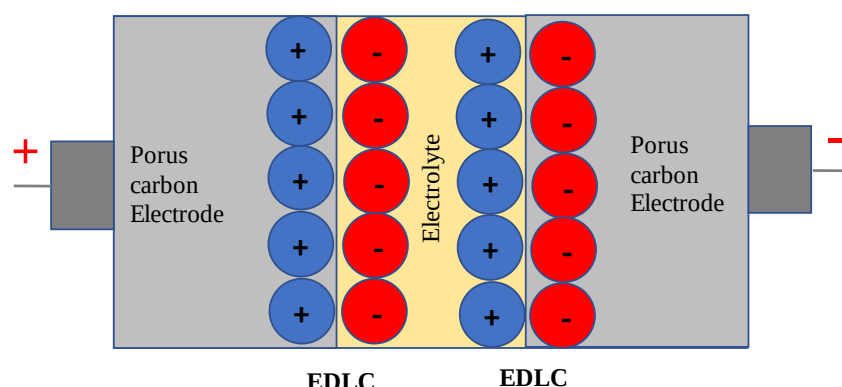


Figure 2. Schematic of basic EDLC supercapacitors.

Energy Density $E = \frac{1}{2} CV^2$	
C= Capacitance can be increase by 1. Electrical conductivity 2. Pore size 3. Surface area 4. Functional group	V=Voltage can be increase by 1. Ionic liquid 2. Organic electrolyte 3. Asymmetric supercapacitor 4. Battery Super capacitor hybrid

Figure 3. Parameters for enhancing energy density of supercapacitors.

Pseudocapacitor

Works on Faradaic redox reaction for storing the charge at the electrode, the charge that occurs between electrode and electrolyte. A schematic of a pseudocapacitor is shown in Figure 4. There are Faradic processes like reduction-oxidation, intercalation, and electrosorption process [11–13] that help pseudocapacitors attain higher capacitance value and specific energy than EDLCs [14–16]; however, lower operating voltage, compared to EDLC, limits their actual energy density also lower power density, limited life cycles, and expensive electrode materials than EDLC has caused hindrance in its wide acceptance. More often conducting polymer and metal oxides are used as electrode materials for storing charge.

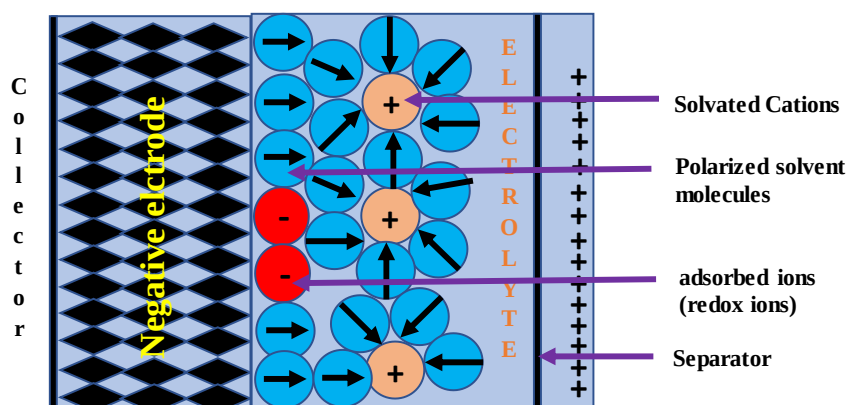


Figure 4. Schematic of pseudocapacitor.

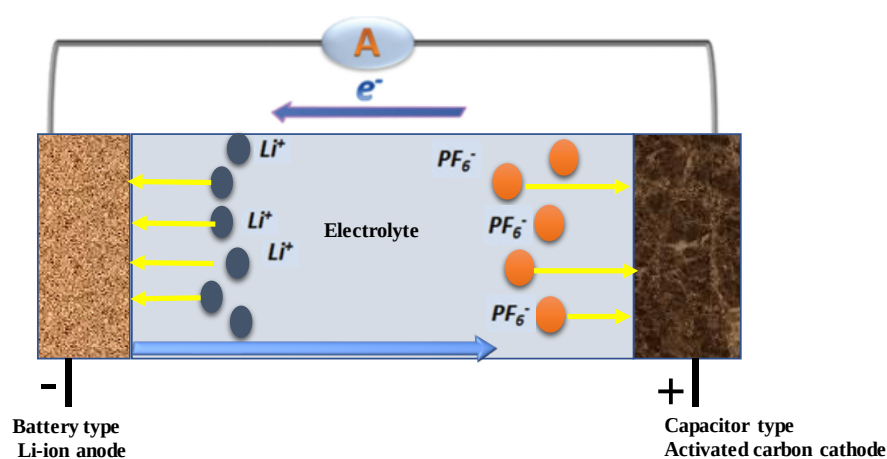


Figure 5. Schematic of hybrid capacitor.

Hybrid Supercapacitor

It is an amalgamation of EDLCs type supercapacitors and pseudocapacitors, thus offering similar power density as that of EDLCs and specific energy like pseudocapacitors. The Schematic of a Hybrid Capacitor is shown in Figure 5. For storing charge, it follows both the Faradaic and non-Faradaic processes. The best example is lithium-ion hybrid capacitor (LIHCs) which is leading the market [17]. Advancement in technology requires a hybrid capacitor as it offers a bridge between LIBs and EDLC supercapacitors. It comprises one electrostatic electrode and the other is an electrochemical electrode. Hybrid capacitors offer the advantages of LIBs (like high energy density, reduced self-discharge) and supercapacitors (like high power density, better safety in terms of thermal run away at a higher temperature, more charge-discharge cycles, less performance degradation over the period of time, super-fast charging, etc.). It comprises positive and negative electrodes, where the former is made up of activated carbon immersed in a liquid electrolyte (lithium-ion salt) and the latter part is made up of carbon-based material doped with lithium-ion. A separator in between avoids the direct electrical contact of two electrodes. Pre-doping of the electrode helps to stabilize the electrode potential, i.e., lesser will be the self-discharge, which is one of the major drawbacks of existing supercapacitors. Also, the electrical potential at the negative electrode will be reduced if it is pre-doped with lithium ions, which means a higher output potential to be derived without high potential at the positive electrode, (till 3.8 V). As the specific energy of the capacitor is related to the square of the voltage; hence, Hybrid capacitors are several times denser than EDLC with similar power density. The endurance limit considering charging and discharging cycles in a hybrid capacitor is much beyond LIBs, as ions in lithium-ion capacitors are simply adsorbed or desorbed on the electrode surface, hence there is no crystalline change. Whereas in the case of batteries, ions are intercalated or deintercalated into carbon lattice thus causing the progressive change in crystalline structure with

every charge/discharge. Safety perspective also Hybrid capacitors are safer as it does not have oxygen or oxides, so they are not prone to thermal runaway.

The requirement of specific energy vs. specific power for various supercapacitor can be understood from Figure 6.

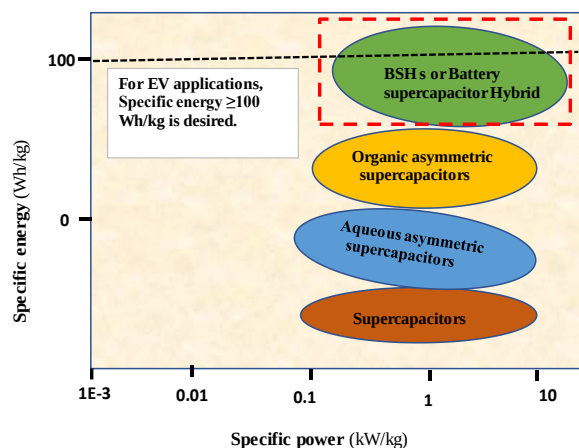


Figure 6. Specific energy versus specific power for various supercapacitors.

CAPACITANCE INFLUENCING FACTORS

Research has been carried out on various influencing factors to enhance the capacitance of supercapacitors. Supercapacitors like EDLC capacitance depend upon their charge layer thickness, the surface area of the electrode, and the dielectric constant. For electrochemical properties, electrode surface area plays a vital role; also, other factors like pores dimension and its structure, electrical conductivity, etc. need more focus to work on [17, 18].

Electrode Surface Area and Pores Dimension

The supercapacitor capacitance value is highly influenced by the specific surface area of electrodes, and this correlation is not linear. Also, a high specific surface area does not ensure higher capacitance. The pore diameter is the place at which charges rest effectively; hence, it is also termed the effective surface area of the electrode. Pore's structure can be categorized as per their diameters for instance micropores (2 nm), mesopores (2–50 nm), and macropores (50 nm). More concentration of micropore and mesopore contribute to higher surface area and thus result in higher capacitance. Pores size of at most 0.4 nm diametrically is insignificant to capacitance [10]. Recently, Gogotsi and Simon [19] illustrated the correlation between pore diameter and electrolyte ion for getting higher capacity. They also mentioned that maximum capacitance can be attained if the electrode pore diameter is less than 1 nm and corresponding electrolyte ions are of the same range [5]. Recently Ruoff and coworkers mentioned that electrode material with activated graphene of surface area up to 2,400 m²/g and orifice diameter of 0.6–5 nm can have specific energy up to 20 Wh/kg based upon device weight (it can be 70 Wh/kg based upon material weight) [20]. Intensive research has been carried out for increasing the capacitance by optimizing pore size, and effective surface area including highly porous carbon [21–23], nanosheets of porous carbon [24, 25], and graphene structure [26, 27]. The selection of electrode pore size and its compatibility with electrolyte ions is a major challenge. As per current research in situ measurement modeling and simulation experiments will help in identifying the best possible electrode pore diameter and its surface area for maximum capacitance. Simulation and modeling experiments help in making electrodes select the correct pore shape, and size, and pores distribution can be tailored for increasing the specific energy of the supercapacitor with no trade-off for specific power and cycle life. Electrode's technology should be developed in such a way that it should be environmentally friendly, store more charge, cheaper to manufacture on a large scale along with the capacity of faster charge and discharge electrical load. Using carbon-rich materials and then drying in low-density aerogel is a novel method of electrode preparation. Aerogel itself can act as a crude

electrode, and thus double the capacitance by above mention method. Aerogels used are wet and gel kind of materials that undergo drying and heating to replace their liquid content with air or other gas. The advantage of this method is aerogel 3D structure will be retained which gives enhanced surface area and extremely low density. One gram of aerogel surface area is equivalent to or more than the surface area of a football field. Aerogels are generally made from gel-like polymers created from formaldehyde and other carbon-rich molecules. Carbon-rich electrodes have a high effective surface area, which can be synthesized from basic inexpensive base materials when it is coupled with a streamlined synthesis process then higher production volume can be produced at a cheaper rate. Aerogels are mixed with materials like molybdenum disulphide or tungsten disulphide, which is being used as industrial lubricants. These lubricants break into thin sheets using high-frequency sound waves, they were then incorporated into a carbon-rich gel structure. This method is very fast and takes hours to produce fully loaded wet gel compared to other methods which may take many days. Adhesives and other carbon-rich materials will be added with dried and low-density aerogel to form “Dough” which subsequently then be processed for use. Electrode produced from the above process offers a capacitance of at least 127 percent more than carbon-rich aerogel alone. Its performance can be further scaled up by combining aerogels with sheets of molybdenum disulfide or tungsten disulfide of thickness less than 10 to 100 atoms thick.

Surface Functional Groups

Heteroatoms like nitrogen (N_2) and oxygen (O_2) considerably increase the capacitance by increasing the wettability of the electrode surface which assist in faradic redox reactions. Recently Huang et al. [28] mentioned that carbon with a mesoporous structure doped with nitrogen content (8.2–11.9%) offers specific energy of 41 Wh/kg depending upon device weight. In two ways, nitrogen-doped carbon materials can be produced, posttreatment and in situ simulation method. According to the posttreatment method, pyrrole, NH_4OH , and/or NH_3 can be treated with carbon structures like nanofiber [29], metal-organic framework/graphene aerogel [30], oxides of graphene [31] to produce N-doped electrode. In the in-situ methods, various nitrogen-rich forerunners are used to produce polypyrrole [32] and nitrogen-doped carbon materials, polyacrylonitrile [33], and nitrogen-rich ionic liquids [34]. To make this cost-effective technology, many carbon elements are synthesized from natural sources which are cheaper and have various resources with environmentally friendly [35–43]. Porous carbon nanosheet doped with nitrogen (HPNC-NS) is enriched with nitrogen doping (4.7%) and enhanced surface area of $2494\text{ m}^2/\text{g}$ as it is extracted through natural silk. The extremely large energy density of range 102 Wh/kg and specific capacity of 242 F g^{-1} were observed in EMIMBF₄ ionic liquid (IL) electrolytes. Nitrogen doping greater than 15% reduces the capacitance and cycling performance due to a decrease in conductance. Substantial research is going on for designing various functional groups for electrodes, still, there is a limitation in evaluating capacitance value on the basis of functional groups present. More focus is required to establish a correlation between capacitance and functional groups for increasing the capacitance.

Novel Materials

Research and development are required for materials that either can be used as an electrode or as a coating layer over the electrode to improve the specific surface area and its electrical conductivity. The porosity and effective surface area of metal-organic frameworks are much more advanced than activated carbon, thus challenging the carbon electrode roles in EDLCs [44], but due to the low electrical conductivity of MOFs, its usage as an electrode for EDLCs was hindered. Dinca et al. [39] unveiled MOF $Ni_3(HITP)_2$, which can be a potential stuff for EDLCs electrode as it is having higher electrical conductivity. A specific capacity of $\sim 18\text{ }\mu\text{F cm}^{-2}$ was attained with no consideration of conductive materials and binders. The aforementioned capacitance value is much greater than carbon-based electrodes. Thus, EDLCs can be extended further by tailoring materials' properties through their increased specific surface by architecture or porous distribution and electrical conductance by using binders. For the future, advanced research work in the area of material design like optimized surface area, pore size, and deliberately introducing heteroatoms into MOFs structure has to be considered for better performance. The examples of various electrodes and electrolytes for EDLC performances are given in Table 2.

Table 2. Various electrodes and electrolytes for EDLC performances [45].

Electrode	Electrolyte	Surface area (m ² g ⁻¹)	Capacitance C(Fg ⁻¹)	Potential (V)	Energy density (Wh/kg)
Mesoporous carbon	Li ₂ SO ₄	1580	740	1.6	63
Activation of graphene	BMIMBF ₄ /AN	2400	166	3.5	70
Holey graphene	EMIMBF ₄ /AN	1560	298	3.5	127
Hierarchical carbon	BMIMPF ₆ /AN	2582	207	3.5	89
N-doped porous carbon	EMIMBF ₄	2494	242	3.5	102
Porous carbon nanosheet	EMIMBF ₄	3326	244	3.5	104
Porous carbon flake	EMIMBF ₄	3301	246	3.5	103

Working Voltage

Apart from capacitance, the working voltage also contributes to specific energy as voltage square is corresponding to specific energy ($E = 1/2CV^2$). Generally, a supercapacitor has a low energy density as it comprises of aqueous electrolyte whose voltage is less than 1.0 V. On the contrary, organic electrolytes are having more operating voltage than 2.0 V. In the case of an IL electrolyte system these operating voltage can reach beyond 3.0 V, which is comparable to conventional lithium-ion batteries. ILs are more promising electrolytes for attaining higher working voltage as their electrochemical stability ranges from 2.0 to 6.0 V. Well defined ion size of ILs electrolyte can be selected due to the absence of solvent and it can be designed compatible with electrode porous distribution to increase the performance of supercapacitor. Recently, Cao et al. [40, 41, 46] manufactured the carbon structure with reform pore size using the “puffing effect” showing the porous structure of 0.7 nm yield maximum specific capacity [19]. For ILs EMIMBF₄ upper limits of BF₄⁻ ions are 0.48 nm and for EMIM⁺ ion is 0.76 nm specific energy of 103 Wh/kg can be obtained using a porous carbon structure of specific capacity value (246 Fg⁻¹) when coupled with high voltage ILs electrolyte (EMIMBF₄) 3.5 V. However major drawback for ILs is they are highly viscous and has less ionic conductance causing a detrimental effect in its specific capacity. It can be offset by adopting electrolytes having both ILs and organic. Duan et al. [19] used an EMIMBF₄/AN mixture of electrolytes and claimed a high specific energy supercapacitor, i.e., 35 Wh/kg depending upon device weight and of operating voltage 3.5 V. There is a probability of increasing energy density of supercapacitor by increasing the working voltage. In the future, extensive research is required in designing electrolytes possessing characteristics properties of higher working voltage, high ionic conductivities, maintaining a less viscous nature for a wide range of temperatures, and optimal ionic radii. Though numerous factors influence specific energy. Maximum specific energy is not possible solely by addressing a single issue, as the above-mentioned various factors contribute to improvement. It is required to understand in detail and investigate the influencing factors and their issues simultaneously.

Asymmetric Supercapacitors

These are the capacitors, in which two dissimilar electrode materials offer the unique advantage of broad voltage increases its specific energy. Normally, oxides of metals like MnO₂, Ni(OH)₂, and RuO₂ are considered as one electrode [47–58] whereas permeable carbon [59] is used as other electrode stuff for the asymmetric supercapacitors (ASCs). The electrolyte used in ASCs is an aqueous electrolyte having a potential range greater than the voltage of 2. Specific energy up to 100 Wh/kg [60–62] can be reached in such ASCs. Thus, higher specific energy for ASCs can be gained by using the higher working potential of electrolytes like organic or ILs. Recently Misra et al. [63] used tandem ASCs of potential 4.5 V having specific energy more by 61% higher than single ASCs. However, pseudocapacitor structure gets affected due to continuous electrochemical reactions thus hampering their stabilities.

Materials for Negative Electrode

ASCs should be designed considering the negative electrode of carbon base material, which is low in cost, abundant in nature, nontoxic, and most important high electronic conductivity. Carbon-rich

materials like activated carbon, carbon nanotube, graphene, etc. have drawn worldwide interest. ASCs with the negative electrode of activated carbon and the positive electrode of metal oxides like MnO_2/SiC having nanoneedle composites were designed by Kim et al. [64]. These ASCs have operating potential ranges from 0–1.9 V and their corresponding specific energy of 30 Wh/kg. Similarly, Qiu et al. [65] have designed a 3D electrode with a vertical alignment of CNTs on carbon fibers thus producing enhanced specific energy of 70 Wh/kg, it has a remarkable 97% holding capacity despite of 20,000 charge/discharge cycle. Graphene exhibits unmatched electrochemical reactions than activated carbon and carbon nanotubes due to superior properties like (higher effective surface area, higher conductivity, and higher durability). Liu et al. [66] have given a distinctive design concept of bend morphology which will not allow nanosheet palletizing; thus, resulting in mesopores emergence which will be approachable to electrolyte ions. Hence, expand its specific energy to 90 Wh/kg.

Materials for Positive Electrode

For ASCs, metal oxides like Ruthenium oxide, nickel hydroxide, and Manganese dioxide are mostly preferred for positive electrode material owing to their higher potential window and specific capacitance. Recently, Kaner et al. [67] claimed for a supercapacitor has three-dimensional porous Ruthenium oxide nanoparticles hitched to a graphene sheet. Such electrodes delivered an extensive capacity of 1139 Fg^{-1} . The specific energy of ASCs having graphene sheets hitched with Ruthenium oxide as a cathode and (AC) as an anode is in the range of about 55 Wh/kg and a corresponding power density of about 12 kW kg^{-1} . However, MnO_2 has a major drawback of poor electronic conductivity and lower surface area which has limited its practical usage. This issue can be well addressed if nanostructured MnO_2 is used with more surface area and conductive materials. Wu et al. [68] examined the performance of ASCs using Manganese dioxide nanowire and graphene combination as cathode and for anode graphene in sodium sulphate aqueous solutions. The operating potential range of the above configuration ASCs is from 0.0 to 2.0 Volt and the corresponding specific energy of 30.4 Wh/kg is based upon the active elements' weight. Ruoff et al. [69] designed composites of nickel (II) hydroxide with ultrathin graphite without binder, here 3-dimensional ultrathin graphite exhibit high porousness and electrical conductivity. ASCs using nickel (II) hydroxide with ultrathin graphite as cathode and graphite oxide as anode shows a specific power output of 44 W/kg more than existing traditional and commercially available supercapacitors. For successful implementation of a supercapacitor in automotive, Its Energy density should be of range at least 100 W h/kg . For this along with ASCs of wide working voltage, advancement in electrode materials and design is required to have a higher surface area, higher electrical conductivity, and good ion diffusion path. The synergies effect of composites made by the amalgamation of various capacitive materials should be worked upon which can enhance the surface area, extreme porousness, better ionic conductivity, and broader working voltage. Extensive research work is required in the synergy effect area to explore the possibility of making the energy density of supercapacitors comparable to LIBs.

BATTERY SUPERCAPACITOR HYBRID (BSH): FUTURE PROSPECTS FOR E-MOBILITY

Electric vehicle adoption can help in decarbonizing the planet and in reducing the catastrophic effect of global warming. However, for its faster adoption, EVs should offer a higher driving range, faster charging/discharging rate, safety, long cycle life, and last, but not least, lower buying cost. With current available LIBs technologies, driving range, and fast charging can be gained but at the expense of less battery life, safety issue, and higher cost. Thus, there is a need for energy storage like BSHs which can offer all the aforementioned benefits. BSH it is an amalgamation of Libs and supercapacitors which exhibit the high specific energy of LIBs and the specific power of supercapacitors. Thus, taking the cumulative benefit of LIBs and supercapacitor and eradicating the negative effects of both. BSH has one high-capacity electrode similar to the battery-type and the other is a high-rate capacitive electrode. BSH advantages make it suitable for applications where enhanced specific energy (wide potential and capacity) and enhanced specific power are required like EVs [70,

71]. BSH has been classified on the basis of electrodes and electrolytes like Li-ion, Na-ion, Zn-ion, alkaline, etc.

Li-ion BSH

In this type of BSH, a lithium-ion electrode will be used because of its high energy density. Lithium-ion BSHs offers the advantages of both supercapacitor and LIBs thus they can be employed as a potential source of energy for future EVs. Nanostructured battery-type electrodes help in increasing performance. Lim et al. [72] claimed BSHs of specific energy 63 Wh/kg using Niobium pentoxide at carbon nanocrystal anodes. In Li-ion BSHs, the cathode used is an intercalation battery-type and the anode is a capacitive carbon type are having higher working potential, because of the high voltage band of cathode Xia et al. [73] unveiled parity of aqueous Li-ion BSHs made up of AC and Lithium manganese oxide, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and LiCoO_2 . According to his claim BSHs device energy storage kinetics is slow due to the pristine behavior of the intercalation cathode, which limits the specific energy storage at around 40 Wh/kg and specific power output at 900 W/kg respectively. To offset low energy issues, the nanostructure can be used to increase performance. Yu et al. [74] constructed lithium-ion hybrid capacitor using nitrogen-doped Li_3VO_4 carbon nanowires with offers specific energy of 136.4 Wh/kg and specific power output of 532 W/kg depending upon active material weight. Remarkable work done by Sun et al. [75] asymmetric hybrid Li-ion BSHs exhibiting specific energy of 222 Wh/kg and specific power output of 410 W/kg. Above BSHs has Lithium-ion battery-type anode and cathode as EDLC type. Anode and cathode were designed using carbon nanotubes of single-wall and sulfonated graphene (SG) composites. The above electrodes assist in avoiding the piling up of nanosheets of graphene thus improving specific energy along with the electrical conductivity of electrodes. Anode will be electrochemically pre-lithiated which enables electrode performance for a higher amount of lithium insertion and de-insertion. Also, the advantage of BSHs with asymmetric graphene electrodes is to increase operating potential differences, which in turn increase specific energy. However, usage of limited and costlier Lithium will result in higher ownership costs and future supply risk to meet the demand. Thus, there is a need to switch to multivalent anodes like materials Na^{1+} , and Zn^{2+} .

Na-ion BSH

For sodium-ion BSHs, utilization of carbon for both anode and cathode was explored widely. This device used capacitor electrode-type carbon as a cathode while intercalation carbon as an anode. The electrochemical properties of Na-ion BSHs are very low due to the reduced space of carbon in sodium-ion electrolytes. To improve the efficiency, research on electrode structure at the micro/nanostructure level is required. Ding et al. [76] claimed a carbon electrode for sodium-ion BSH employing carbon materials with flakes, thin and highly porous can exhibit specific energy around 201, 76, and 50 Wh/kg similarly specific power output around 285, 6500 and 16500 W/kg based on active material. For sodium-ion hybrid capacitor, various electrodes of Na-ion were used as battery electrode-type electrodes, for example, Xia et al. [77] claimed hybrid capacitor with carbon-coated Fe_3O_4 nanorod array as anode and $\text{Na}_{0.5}\text{MnO}_2$ nanosheet as cathode offering energy density of 81 Wh/kg and power density 647 W/kg. Alike lithium-ion and sodium-ion BSHs, it is quite difficult to prepare potassium ion hybrid capacitors due to limitations of potassium ion insertion battery-type electrode, as potassium ionic radii are more than lithium- and sodium-ion and due to its scarcity.

Zn-ion BSH

This multivalent zinc ion hybrid supercapacitor can be a promising solution for energy storage for future E-mobility as it offers higher specific energy similar to LIBs and the specific power output of supercapacitors. Using multivalent Zn as an anode, which is abundant in nature, and biodegradable carbon as a cathode can help in attaining high specific energy equivalent to LIBs. Though there is a limitation of a wide operating temperature range, it can be countered by utilizing thermally stable and anti-freeze electrolytes which will also be compatible with advanced cathode materials. Guoshen et al. [78] devised a ZHSC having a cathode made up of activated carbon derived from coconut, and aqueous zinc perchlorate $\text{Zn}(\text{ClO}_4)_2$ electrolyte can offer specific energy of around 190.3 Wh/kg at

89.8 W/kg. Through simulations and experimental data, it was found that zinc perchlorate assists in faster ionic movement than other related Zn salt also it exhibits better anti-freeze properties. Recently Shengnan et al. [79] carry out their research work of attaining enhanced specific energy of ZHSC by 383.2 Wh/kg at 16.8 kW/kg specific power output. Extensive specific energy is possible by adding the multifunctional additive 1-methyl-1-ethyl pyrrolidinium bromide with ZHSC. This results in uniform Zn-ion deposition due to MEP⁺, a rise in capacity because of instant reversible electrochemical reactions of Br₂/Br⁻. Considering the above benefits ZHSC can be the best replacement for currently available LIBs.

Acidic BSH

Utilization of conventional acidic batteries along with supercapacitor called acidic battery super hybrid capacitor. The performance of the lead-carbon combination is superior to other existing BSHs as it has a higher operating voltage range of about 2 volts. Additionally, reprocessing of sulphuric acid and lead oxide has presently become commercially cheap. Lower specific energy (15–30 Wh/kg) and specific power output because of reduced active sites of lead oxides for electrochemical reactions which significantly affects redox reactions.

Alkaline BSH

Alkaline BSHs employ electrolytes of aqueous alkaline and carbon material for the capacitor-type electrode, whereas oxides of transition metal and hydroxides for the second electrode show performance similar to a battery. Lou et al. produced NiMoO₄ nanosheets/nanowire electrodes on different substrates. The combination of NiMoO₄/AC alkaline BSH rendered enhanced specific energy and specific power of 60.9 Wh/kg at 850 W/kg, and 41.1 Wh/kg at 17001 W/kg respectively [80]. For cheaper and environment-compatible iron oxides could be the promising materials for anode materials of alkaline batteries like Ni-Fe batteries as iron is available in abundance. But the applicability of Fe₂O₃ in alkaline hybrid supercapacitors was not explored much due to its poor conductivity and reduction in size either with repeated cycles or with high volume expansion due to higher current usage at charge/discharge cycles. Li et al. showcased an iron oxide-carbon nanorod array anode, in this carbon coating was followed for avoiding structural change and volume expansion thus maintaining the electrode integration in one way and improving its electrical conductivity in another way. However, there are still challenges for deploying the BSHs for broader applications and require extensive research and development in their key area of specific energy storage as well as specific power output as alkaline BSHs still lacks far behind advanced LIBs. Challenges and some of the technological advancements requires for future BSHs are enclosed. (a) Battery-type electrodes generally exhibit less power density due to their slow redox reactions. It can be mitigated by designing electrodes with nanostructure, this will cut down the ion traveling route, along with nano coating with conductive species to improve conductivity and steadiness. For this future research area can be doping in the nanoscale range for increasing the power density. (b) Alternative materials advancement for electrolyte and for anode/cathode, especially for green Na-ion BSHs to get combined specific energy storage and specific power output. Various research tools like simulation, modeling, and computational approach can be utilized for designing electrode and electrolyte materials.

CONCLUSION

In this paper, all aforementioned discussion was related to recent research associated with designing efficient supercapacitors and BSHs. There are various factors or parameters like anodes, cathodes, pore size, surface area, high voltage electrolytes, etc. can be worked upon to tweak the specific energy and specific power output for supercapacitors and make it workable accordingly. However, for electric vehicle application, only BSHs has the potential to revolutionize EV mobility and can replace the ongoing trend of LIBs which uses a rare and costlier raw material. For the future, potential measures are enlisted. Firstly, exploring alternative advanced materials for electrodes and electrolytes is important regardless of the types of supercapacitors. Also, to make BSHs adoption commercially viable, it is required to explore biodegradable materials like bamboo leaves, aloe vera, etc., and other

water-content leaves with combinations of electrolytes having higher operating voltage as mentioned in this paper can be combined and evaluated for performance parameters. It requires various experimental, and computational investigations such as theory, modeling, and simulations that can direct for designing of electrode and electrolyte materials. Future research should be focused on increasing the capacitance by enhancing effective surface area, orifice size, capacity optimization, and having surface functional groups for increasing pseudo-capacitance contribution. Utilizing ILs electrolytes which possess voltage beyond 3 volts, may contribute to higher specific energy. Synchronization between diverse factors is required to understand as it can be a major breakthrough. However, understanding the compatibility between electrode orifices and electrolyte ion is a major challenge. As per the latest updates, in situ experiments modeling and simulations integrations can support predicting the optimized orifice dimensions and its distribution, volume, and electrolyte ion to attain maximum energy density. Similarly, for BSHs, offsetting the slower redox reaction of its battery-type electrode has limited its use for higher power applications. Approaches of nanostructure electrode designing can reduce the ion transport path and coatings at the nanoscale with conductive species for increasing the conductivity can improve conductivity and steadiness. As per current testing, asymmetric BSHs can exhibit specific energy of up to 222 Wh/kg and specific power output of 410 W/kg, using lithium doping in the anode and graphene in the cathode. Here both electrodes are made up of a single carbon nanotube. Advancement in research has brought specific energy factor of BSHs next to LIBs which is being used in the current electric vehicle. Employing BSHs in the electric vehicle could be the best solution for higher range, super-fast charging, safety, and longer service life, which may be equal to vehicle life, whereas for LIBs fast charging is detrimental to safety and service life. Thus, for the future scope of work, BSHs application in EV can be modeled and checked in MATLAB using Simulink or other simulation models for performance comparison with LIBs. Also, the potential of biodegradable materials like coffee beans, coconut fiber, neem, hemp, Ashoka, Aloe vera, etc. can be explored for capacitor-type cathode and recyclable abundant material like Silicon with Magnesium, zinc, Sulphur, etc. for the anode. BSHs can be prepared at the lab using these combinations and tested results of parameters like SOC (state of charge), voltage, service life, charge/discharge characteristics, etc. can be directly compared with lithium type hybrid supercapacitors at part level or else the same can be fed to MATLAB simulations for evaluating performance and efficiency of electric vehicle model. Research on alternate materials to replace lithium from BSHs can help in bringing down the higher cost and easy commercialization of BSHs. It could be the probable solution for future mobility. Thus, BSHs can be considered the best alternative to LIBs in EVs application because of the benefits in the longevity of cycle life, improved energy density, power density, rapid charging, and last but not least improved safety.

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