



The way to improve the energy density of supercapacitors: Progress and perspective

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ABSTRACT Compared with other energy storage devices, supercapacitors have superior qualities, including a long cycling life, fast charge/discharge processes, and a high safety rating. The practical use of supercapacitor devices is hindered by their low energy density. Here, we briefly review the factors that influence the energy density of supercapacitors. Furthermore, possible pathways for enhancing the energy density *via* improving capacitance and working voltage are discussed. In particular, we offer our perspective on the most exciting developments regarding high-energy-density supercapacitors, with an emphasis on future trends. We conclude by discussing the various types of supercapacitors and highlight crucial tasks for achieving a high energy density.

Keywords: energy materials, supercapacitor, capacitance, working voltage, energy storage

Green energy storage gadgets and technology have become significant because of severe energy and environmental concerns. Presently, commercially available energy storage devices mainly include Li-ion batteries and supercapacitors [1,2]. Li-ion batteries (LIBs) have been used in many practical applications, such as power supplies for portable devices and electric vehicles (EVs), because of their high energy density [3,4]. The highest EV running distance is over 500 km. However, the drawback of EVs is the long charging time of up to several hours, which limits the EV's mobility. Therefore, selecting an appropriate energy storage device is crucial for large-format applications, such as EVs (Fig. 1).

Supercapacitors have the advantages of high power density, safety, a broad range of operating temperatures, and superfast charge times [5]. The charging time for a supercapacitor generally ranges from a few seconds to minutes, and the typical cycling life can reach 100,000 cycles with only a slight performance degradation. These aforementioned technological features

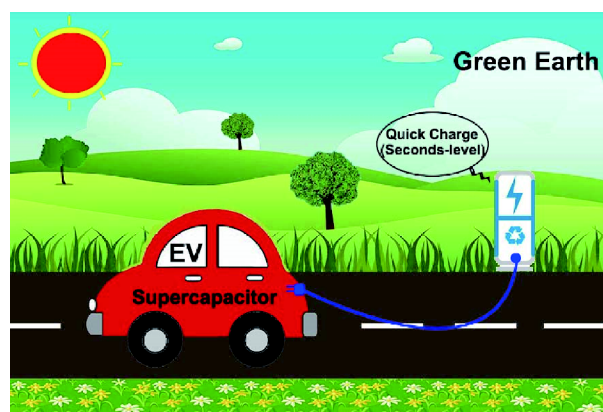


Figure 1 Schematic illustration of future supercapacitors device for EVs.

allowed supercapacitors to become the next generation of energy storage devices. However, they still have low energy densities.

The energy density of standard supercapacitor devices is limited to 10 W h kg^{-1} [3]. Thus, supercapacitors are presently only used as EV starters and cabin door switchers for airplanes, which require a high power density and a short discharge time. The first advantage of using supercapacitors as EV power suppliers is their long cycling life (Table 1), which is superior to the lifetime of LIBs, which is generally 2,000 times, or 5–6 years if the device is charged once daily. However, the lifetime of supercapacitors is much greater than ten years. Furthermore, supercapacitors have a rapid charging time of several minutes or less, which is much less than the time required to fill oil. The bottleneck is the running distance (energy density), which should be at least 100 km for use in EVs. Thus, the energy density must also be greater than 100 W h kg^{-1} . In this case, the mileage goes to infinity with negligible charging times. EV mobility can be greatly

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Table 1 Comparison of performances of supercapacitor and battery

Performance	Supercapacitor	Battery
Mechanism	Physical or chemical	Chemical
Safety	★★★★★	★★★☆☆
Charge time	Short (seconds-level)	Long (hours-level)
Cycling life	Long (>10 ⁵ cycles)	Limited (~10 ³ cycles)
Power	High (>10 ⁴ W kg ⁻¹)	Low (~10 ³ W kg ⁻¹)
Energy	Limited (<10 W h kg ⁻¹)	High (~200 W h kg ⁻¹)

enhanced using supercapacitors whose performance is competitive with LIBs.

From this perspective, we briefly summarize the state-of-the-art achievements that have increased the energy density of supercapacitors and the crucial remaining challenges for developing high-performance supercapacitors. In addition, we highlighted the relevance between the energy density and key routes, such as the capacitance and working voltage. By summarizing crucial factors, such as the surface area, pore size, surface functional groups, high-voltage electrolytes, and various supercapacitor device configurations, we aim to provide a summary of recent progress of high-energy-density supercapacitors and identify pathways for developing further advancements in high-energy-density supercapacitors.

WORKING PRINCIPLES OF SUPERCAPACITORS

Supercapacitors generally comprise two types. The first type is known as the electric double-layer capacitor (EDLC), in which the electrode–electrolyte interface offers capacitance by accumulating electrostatic charges. Hence, the capacitance intensively depends on the effective surface area of the electrode. The other type is the pseudocapacitor, which has electrochemical reactions at the electrode [6]. Thus far, EDLC supercapacitors typically comprise porous carbon electrodes. These have energy densities that are less than 10 W h kg⁻¹, because of the low specific capacitance (less than 200 F g⁻¹), and low operating-potential windows that are less than 1.0 V. The device can be considered as two capacitors attached in series because every electrode–electrolyte interface stands for a capacitor [7]. The capacitance is the sum of two electrodes. The capacitance (C_{dl}) of every interface is given by $C_{dl} = \epsilon A / 4\pi t$, where ϵ is the dielectric constant, A is the effective surface area, and t is the thickness of the electrical double layer. The energy density (E) and power density (P) are calculated as follows: $E = 1/2CV^2$, $P = V^2/4R$, where C is the DC capacitance, V is the voltage, and R is

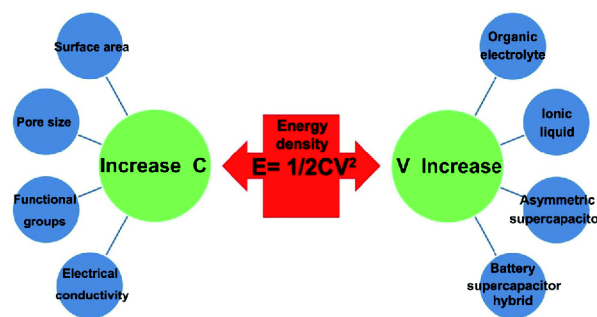


Figure 2 Schematic illustration of various routes to increase energy density of supercapacitor.

the resistance [8]. According to this equation, much research has focused on enhancing the energy density of supercapacitors by improving their capacitance and working voltage; the crucial factors for achieving this are presented in Fig. 2.

CRUCIAL FACTORS INFLUENCING CAPACITANCE

Considerable research efforts have been devoted to optimizing the structure-influencing factors to achieve high capacitance. The capacitance of EDLCs depends on the surface area and the thickness of the electric double layer and the dielectric constant. The electrochemical properties mainly relate to the electrode surface area. Some other factors, for example, pore size and structure, surface functional groups, and electrical conductivity, require additional attention. [9,10].

Specific surface area and pore size

Increased capacitance is generally associated with higher specific surface areas, but this trend is not linear and a higher surface area does not guarantee increased capacitance. The specific surface area where the charges can be absorbed is termed the effective surface area, which is related to the pore diameter. Pores can be defined according to their diameter as micropores (2 nm), mesopores (2–50 nm), and macropores (50 nm). Generally, higher abundances of micropores and mesopores result in higher specific surface areas. However, the specific surface area associated with pores with diameters of less than 0.4 nm may not contribute to the capacitance [8]. Recently, Simon and Gogotsi *et al.* [11] demonstrated the relationship between the true pore size and the ion for obtaining the maximum capacitance. Furthermore, they reported an exceptional property enhancement for electrode materials with pore sizes of less than 1 nm and

found the maximum capacitance when the material's pore size was approximately similar to the size of the electrolyte ions [5]. A strong debate remains regarding the optimal pore size and surface area for enhancing electrode properties. Recently, Ruoff and coworkers reported activated graphene with a surface area of up to $2,400 \text{ m}^2 \text{ g}^{-1}$ and pore widths of 0.6–5 nm, which have an energy density of up to 20 W h kg^{-1} depending on the device's weight (70 W h kg^{-1} based on the active material weight) [12]. In addition, recent breakthroughs have achieved improved capacitance through optimizing the surface area and pore structure of carbon electrodes, including highly porous carbon [13,14,15], porous carbon nanosheets [16,17], and holey graphene frameworks [18,19]. These materials have established future trends in the use of carbon electrodes. The effects of the surface area and pore size have clearly driven the research efforts toward understanding the electrolyte ion in pores. However, it remains a tremendous challenge to fully understand the interaction between the pores and electrolyte ions. Considering recent progress, *in situ* measurement experiments coupled with modeling and simulations will help determine the relevant mechanisms for predicting the optimal surface area and pore size for maximal capacitance. Moreover, controlling the pore size distribution and structure remain challenging. *In situ* experiments and modeling/simulations suggest that fabricating electrode materials with narrow pore size distributions and proper pore structures would increase the energy density of supercapacitors without decreasing the high power density and long cycling life.

Surface functional groups

Besides the aforementioned effective surface area and pore structure properties, surface functional groups, or heteroatoms (N, O), can also significantly affect the capacitance properties. This is because they can enhance the wettability of the electrode surface and provide extra capacitance resulting from faradaic redox reactions. Recently, Huang *et al.* [20] reported nitrogen-doped mesoporous few-layer carbon with a high N content (8.2–11.9%). These resulting mixed materials can have an energy density of 41.0 W h kg^{-1} depending on the device's weight (63.0 W h kg^{-1} based on the active material's weight) in a $2 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$ aqueous electrolyte. Therefore, introducing surface functional groups appears to effectively increase capacitance. Nitrogen-doped carbon materials are synthesized *via* two main methods: posttreatment and *in situ*.

In the posttreatment method, various carbon struc-

tures, such as nanofiber [21], metal-organic frameworks (MOFs)/graphene aerogel [22], and graphene foam/reduced graphene oxide [23], can be treated with pyrrole, NH_4OH , and/or NH_3 to obtain N-doped electrodes. In the *in situ* preparation method, different N-containing precursors are used to synthesize N-doped carbon materials, including polypyrrole [24], polyacrylonitrile [25], and nitrogen-containing ionic liquids (ILs) [26]. Moreover, many functional carbon materials are directly derived from natural resources that are of low cost, have numerous sources, and are environmentally friendly [27–35]. Typical examples of reported EDLC performance are shown in Table 2. Cao *et al.* [27] previously reported N-doped porous carbon nanosheets (HPNC-NS) derived from natural silk. HPNC-NS has a high degree of N-doping (4.7%) and a large specific surface area ($2,494 \text{ m}^2 \text{ g}^{-1}$). A high capacitance of 242 F g^{-1} and a large energy density of 102 W h kg^{-1} (48 W h L^{-1}) were obtained on the basis of active material weight in EMIMBF₄ IL electrolytes. However, excess nitrogen (approximately greater than 15%) reduces the electrical conductivity and, in turn, decreases the capacitance and cycling performance. Although tremendous research efforts have been devoted to designing various surface functional groups for electrodes, it remains a huge limitation that capacitance values cannot be absolutely evaluated from the functional groups present. To maximize the capacitance, future work should focus on developing an exhaustive correlation and boosting mechanism to understand the relationship between capacitance and the functional group.

Novel kinds of materials

Clear progress in EDLC development originates not only from optimized parameters or preparation methods for carbon, but also from novel material types that can maximize both the surface area and the electrical conductivity. The surface area and porosity of MOFs far exceed those of activated carbon (AC), potentially challenging the leading role of carbon electrodes in EDLCs [36], whereas MOFs conventionally coupled with exhibiting an extremely low electrical conductivity, which has thus far prevented the use of MOFs as electrode materials in EDLCs. Very recently, Dincă *et al.* [37] showed that porous MOF $\text{Ni}_3(\text{HITP})_2$ has a high electrical conductivity and is a promising electrode material for use in EDLCs; a large capacitance of $\sim 18 \mu\text{F cm}^{-2}$ was achieved without the use of any conductive additives or other binders, which is greater than the capacitance achieved using most carbon-based electrodes. Based on

Table 2 Typical examples of reported EDLCs performances

Electrode	Electrolyte	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	$C(\text{F g}^{-1})$	Potential (V)	Energy density	Based on	Ref.
Carbon nanospheres	KOH	2225	230	1.0	/	/	[13]
N-doped carbon nanofiber	KOH	562	202	1.0	7.11 W h kg^{-1}	Device	[21]
N-doped 3D graphene	KOH	583	297	0.8	15.2 W h kg^{-1}	Device	[23]
Functionalized 3D carbon	KOH	2870	236.3	1.0	/	/	[24]
Mesoporous carbon	H_2SO_4	1580	840	1.2	39.5 W h kg^{-1}	Active material	[20]
	Li_2SO_4	1580	740	1.6	63 W h kg^{-1}	Active material	
	Li_2SO_4	1580	740	1.6	41 W h kg^{-1}	Device	
N-rich carbon-graphene	PVA/ H_2SO_4	814	-	1.0	33.89 W h kg^{-1}	Device	[22]
N-rich nanocarbon	H_2SO_4	500	166	1.0	/	/	[25]
Activation of Graphene	BMIMBF ₄ /AN	2400	166	3.5	70 W h kg^{-1} 20 W h kg^{-1}	Active material Device	[12]
Porous carbon nanosheets	TEABF ₄ /AN	2200	150	2.7	30 W h kg^{-1}	Device	[16]
Holey graphene	EMIMBF ₄ /AN	1560	298	3.5	127 W h kg^{-1}	Active material	[18]
Hierarchical carbon	BMIMPF ₆ /AN	2582	207	3.5	89 W h kg^{-1}	Active material	[14]
3D porous networks	TEMABF ₄ /PC	1810	178	2.5	38 W h kg^{-1}	Active material	[19]
Functionalized 3D carbon	(C_2H_5) ₄ NBF ₄ /AN	2870	224.5	2.5	/	/	[24]
Porous carbon	TEABF ₄ /AN	3270	210	2.0	42 W h kg^{-1}	Active material	[32]
Carbon flake	LiPF ₆	1306	126	3.0	45.33 W h kg^{-1}	Device	[28]
Microporous carbon	LiPF ₆	1230	88	3.0	56 W h kg^{-1}	Active material	[35]
Carbon nanosheets	BMPY TFSI	2287	-	3	19 W h kg^{-1}	Device	[17]
Activated graphene	EMIM TFSI	3290	174	3.5	74 W h kg^{-1}	Device	[15]
N-doped porous carbon	EMIMBF ₄	2494	242	3.5	102 W h kg^{-1}	Active material	[27]
3D porous carbon	EMIMBF ₄	2475	196	3.5	70 W h kg^{-1}	Active material	[29]
Porous carbon nanosheet	EMIMBF ₄	3326	244	3.5	104 W h kg^{-1}	Active material	[31]
Porous carbon flake	EMIMBF ₄	3301	246	3.5	103 W h kg^{-1}	Active material	[33]

these developments, EDLCs' capacitance can be further increased both from a material perspective, by designing high-surface-area and high-electric-conductivity materials, and from an engineering perspective, by adding conductive binders and improving device architectures. Various approaches for material design, such as optimized surface area and pore size, intentionally introduce pseudocapacitive heteroatoms into the MOF structure, which can be further developed in the future.

CRUCIAL FACTORS INFLUENCING WORKING VOLTAGE

Except regarding capacitance, the working voltage is very important for the energy density because its square is directly proportional to the energy density ($E = 1/2CV^2$). For the same capacitance, a threefold increase in the working voltage leads to approximately an order of magnitude increase in energy.

The voltage for aqueous electrolyte systems is generally less than 1.0 V, which explains why a normal supercapacitor device has a rather low energy density.

Organic electrolytes have a relatively higher operating voltage greater than 2.0 V. The highest voltage devices were generally realized in IL electrolyte systems, in which the voltage can reach more than 3 V, which is comparable with those of normal Li-ion batteries. Based on their wide voltage windows (>3 V) and high chemical and physical performances, ILs are attractive candidates for next-generation electrolytes.

Using ILs to increase the working voltage is a promising way to achieve high energy densities because of their broad electrochemical stability window that ranges from 2.0 to 6.0 V, especially about 4.5 V. Moreover, ILs without solvation shells can provide well-identified ion sizes due to the absence of a solvent, which enables the with pore sizes of electrodes to be optimized. Very recently, Cao

et al. [31,33] prepared porous carbon with an optimized pore size by taking advantage of the “puffing effect,” which is consistent with previous research whereby 0.7 nm size pores yield the highest capacitance [11]. In the EMIMBF₄ ion liquid electrolyte, the upper limits are 0.48 and 0.76 nm of BF₄⁻ and EMIM⁺, respectively. Stock porous carbon flakes showed a high capacitance (246 F g⁻¹), and coupled with a high-voltage EMIMBF₄ IL electrolyte (e.g., 3.5 V), the energy density was 103 W h kg⁻¹ based on the active material weight. However, ILs typically have a high viscosity and a low ionic conductivity, which decreases the capacitance. To address this, mixtures of ILs and organic electrolytes have become popular. Recently, Duan *et al.* [18] reported high-energy-density supercapacitors based on an EMIMBF₄/AN mixture electrolyte, with an energy density of up to 35 W h kg⁻¹ based on device weight, which can achieve an operating voltage of up to 3.5 V. It is expected that improvements in the working voltage can enable a high energy density. In the future, the most urgent task is to design more appropriate electrolytes that have higher working voltages, high ionic conductivities, optimal ionic radii, and a suitable viscosity over a broad temperature range and an appropriate porous structure to adapt to IL sizes.

Despite several influencing factors on the energy density, the discussion is divided into several sections for clarity, and these factors synergistically improve the energy density. The maximal energy density could not be obtained by only addressing a single issue, unless the aforementioned influencing factors and issues are further investigated and addressed simultaneously.

ASYMMETRIC SUPERCAPACITORS (ASCs)

Asymmetric supercapacitors (ASCs) are assembled using two dissimilar electrode materials that offer the distinct advantage of a wide operational voltage window, which significantly enhances their energy density. Generally, metal oxides are employed as one of the supercapacitor electrodes, whereby RuO₂, MnO₂, and Ni(OH)₂ are the most commonly used materials [38–49]. Other materials can be used as the other electrode to fabricate ASCs, such as porous carbon [50]. For example, ASCs employing aqueous electrolytes have potential windows of greater than 2.0 V. The energy density of ASCs can reach almost 100 W h kg⁻¹ [51–53]. Based on these aforementioned features, a higher ASC energy density can be obtained by utilizing organic or ionic-liquid electrolytes, which have higher working voltages. In contrast, Misra *et al.* [54] reported a tandem ASC with a high working potential of

4.5 V to provide a wider voltage window, which had an energy density that was 61% higher than that of single ASCs. However, repetitive electrochemical reactions affect the structure of pseudocapacitor materials, which significantly affects their stabilities. Moreover, devices fabricated from these material types are difficult to prepare compared to EDLC devices.

Negative electrode materials

Carbon-based materials are the best prospective candidates for negative electrode materials in ASCs owing to their low cost, abundance, nontoxicity, and high electronic conductivity. Among the various carbonaceous materials, AC, carbon nanotubes (CNTs), and graphene have attracted remarkable attention. Kim *et al.* [55] fabricated an ASC with functionalized AC as a negative electrode and MnO₂/SiC nanoneedle composites as a positive electrode. The optimized ASC could operate in a voltage window of 0–1.9 V and exhibited a maximum energy density of 30.06 W h kg⁻¹. Recently, Qiu *et al.* [56] fabricated a 3D electrode structure with vertically aligned CNTs that were directly grown on carbon nanofibers (VACNTs/CNFs), which enabled a high specific energy of 70.7 W h kg⁻¹ (based on the active material weight) and 97% retention, even after 20,000 charging/discharging cycles. Graphene has shown a great combination of desirable performance properties (conductivity, surface area, and mechanical strength), which result in better electrochemical properties compared to AC and CNTs. Liu *et al.* [57] proposed a unique curved morphology that prevents the restacking of graphene nanosheets and enables the formation of mesopores that are accessible to ionic electrolytes, which increases the energy density level to 90 W h kg⁻¹.

Positive electrode materials

Metal oxides have great potential as positive electrode materials. RuO₂, MnO₂, and Ni(OH)₂ are promising candidates for positive electrode materials in ASCs owing to their high specific capacitance and large potential window. Recently, Kaner *et al.* [58] reported interdigitated supercapacitors made of 3D porous RuO₂ nanoparticles anchored to graphene sheets. These electrodes exhibited an ultrahigh capacitance of 1,139 F g⁻¹ with an excellent rate capability. Moreover, ASCs employing graphene sheets/RuO₂ as the positive electrode and an AC negative electrode demonstrated an extremely high energy density of 55 W h kg⁻¹ at a power density of 12 kW kg⁻¹. The low surface area and poor electronic conductivity of MnO₂ are two major problems that hin-

der their practical use. Incorporating nanostructured MnO_2 with other materials of high surface area and electrical conductivity has been extensively investigated to address these issues. Wu *et al.* [59] studied the properties of ASCs employing a MnO_2 nanowire/graphene composite as a positive electrode and graphene as a negative electrode in aqueous Na_2SO_4 solutions. The ASC device based on graphene/ MnO_2 operated in a high potential window of 0–2.0 V and had a high energy density of 30.4 W h kg^{-1} based on the active material weight. Ruoff *et al.* [60] reported a binder-free composite of $\text{Ni}(\text{OH})_2$ with ultrathin graphite (UGF), in which the 3D UGF network had a high electrical conductivity and porosity. ASCs employing $\text{Ni}(\text{OH})_2$ /UGF as the positive electrode and graphite oxide as the negative electrode exhibited a very high power density of 44 kW kg^{-1} , which was much higher than those of many traditional, commercially available supercapacitors.

The energy density of next-generation supercapacitors should be close to 100 W h kg^{-1} . Apart from the wide working voltage window in ASCs, the advance of novel electrodes with rational designs is required to obtain increased surface areas, superior electronic conductivity, and good ion-diffusion channels to achieve maximal energy density. Integrating the various capacitive materials as composites should be further studied to obtain increased surface areas, abundant porosity, good electronic/ionic conductivity, and wide voltage windows *via* synergistic effects. Furthermore, an in-depth understanding of these synergistic effects is required in the future. Considering these advances, a high energy density and real capacitive properties can be achieved by optimizing parameters such as components and the mass loading of electrodes.

BATTERY-SUPERCAPACITOR HYBRID (BSH) DEVICE

Realizing both large energy densities and power densities requires the design of novel materials and improved energy storage device configurations [1]. A promising energy storage device configuration is a battery-supercapacitor hybrid (BSH) device, which comprises one high-capacity battery-type electrode and a high-rate capacitive electrode. This has attracted much attention since the device design provides an opportunity to simultaneously have a high energy density (wider working voltage and larger capacity) at a high power density [61,62]. Based on the variety of electrodes and electrolytes, we classified BSH devices into the following types: Li-ion BSH, Na-ion BSH, acidic BSH, and alkaline BSH.

Li-ion BSH

Due to the high specific capacity of Li-ion-type electrodes, Li-ion BSHs bridged the gap between LIBs and supercapacitors and attracted worldwide attention. The development of nanostructured hybrid battery-type electrodes is a promising avenue for enhancing device performances. Lim *et al.* [63] reported Nb_2O_5 @carbon core-shell nanocrystal anodes and BSHs with energy densities as high as 63 W h kg^{-1} . Li-ion BSHs assembled using battery-type lithium-intercalation cathode and capacitive carbon anode are also advantageous and generally have high working potentials, due to the high-voltage plateau of the cathode. Xia *et al.* [64] provided a comprehensive comparison of aqueous Li-ion BSHs assembled from AC and LiCoO_2 , LiMn_2O_4 , and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. However, the reported devices still had slow energy storage kinetics because of the pristine nature of the intercalation cathodes. As a result, the power densities and energy density were constrained to 900 W kg^{-1} and 40 W h kg^{-1} , respectively. Nanostructures could be adopted to promote an increase in the overall performance. Very recently, Yu *et al.* [65] fabricated Li-ion BSHs with peapod-like Li_3VO_4 /N-doped carbon nanowires, which exhibited an energy density of $136.4 \text{ W h kg}^{-1}$ at 532 W kg^{-1} based on the active material weight.

Na-ion BSH

Carbon/carbon matching has been widely investigated in Na-ion BSHs. Intercalation carbon was used as the anode and capacitive carbon was used as the cathode. However, due to the relatively low capacity of hard carbon in Na-ion electrolytes, the electrochemical properties of the device were poor. The design of the micro/nanostructure of the electrode is essential for improving the device's properties. Recently, Ding *et al.* [66] reported a carbon/carbon Na-ion BSH in which the resulting carbon materials were highly flaky, thin, and porous. This Na-ion BSH presented excellent energy and power densities based on active material weight (201, 76, and 50 W h kg^{-1} at 285, 6,500, and $16,500 \text{ W kg}^{-1}$, respectively). Several other Na-ion battery electrodes have been used as battery-type electrodes for Na-ion BSHs; for instance, Xia *et al.* [67] reported Na-ion BSHs with $\text{Na}_{0.5}\text{MnO}_2/\text{Fe}_3\text{O}_4$ @C, which yielded an energy density of 81 W h kg^{-1} at 647 W kg^{-1} .

It is possible to prepare K-ion BSH devices, which are similar in design to Li-ion BSHs and Na-ion BSHs. Although diverse capacitive electrodes from Li- and Na-ion BSHs may be used, there are still significant challenges in

using K-ion intercalation battery-type electrodes. This is because the ionic radius of K^+ is much larger than those of Li^+/Na^+ and the host materials are scarcely available.

Acidic BSH

Lead-acid batteries were developed over one and a half centuries ago, but they still remain one of the most important commercial rechargeable batteries. The hybridization of lead-acid batteries with SC leads to acidic BSHs. Among the various BSHs, lead-carbon capacitors are superior because of their high voltage (~ 2.0 V). Furthermore, recycling PbO_2 and sulfuric acid is now an optimized and a financially self-sufficient process. The lead-carbon capacitor suffers from a low specific energy density ($15\text{--}30$ W h kg^{-1}) and a low power density due to the electrochemically active surface of PbO_2 , which is low and hinders rapid redox reactions.

Alkaline BSH

Nickel-cadmium (Ni-Cd) batteries have been used for ~ 100 years and are the most mature system of alkaline batteries. Alkaline BSHs refer to the hybrid systems that employ alkaline aqueous solutions as electrolytes and carbon materials as the capacitive electrode. The other electrode is based on transition metal oxides/hydroxides that exhibit battery-like performance. Lou *et al.* synthesized $NiMoO_4$ nanosheet/nanowire array electrodes on different substrates. The resulting $NiMoO_4/AC$ alkaline BSH delivered reasonably high energy and power densities (60.9 W h kg^{-1} at 850 W kg^{-1} and 41.1 W h kg^{-1} at $17,002$ W kg^{-1}) [68]. Iron oxides are one of the few anode candidates for rechargeable alkaline batteries, such as Ni-Fe batteries, because of their low cost, environmental friendliness, and natural abundance. However, the application of iron oxides in alkaline BSHs has rarely been investigated. The shortcomings of Fe-oxide anodes are their relatively low conductivity and pulverization with cycling or at high current densities (large volume expansion). Li *et al.* presented a “carbon shell protection” solution and synthesized an Fe_3O_4 -carbon binder-free nanorod array anode. With facile carbon coating, the volume expansion and the possible structural deformation were effectively restricted, helping to maintain the electrode's integration; the carbon shell also improved the electrical conductivity of the electrode [69].

Thus far, BSH properties, especially the energy and power density, cannot compete with advanced batteries and supercapacitors as most BSH types are still in their primary developmental stage and require vast advancements. Some challenges and future developments for

next-generation BSHs are discussed in the following based on the progress attained thus far. (1) Battery-type electrodes generally have slow redox reactions, which restricts their power properties. Currently, the most common approaches for addressing this problem are to design various nanostructures to shorten the ion transport route and to utilize nanoscale coating with conductive species to enhance the conductivity and steadiness. In addition to these above approaches, future research efforts could be directed to designing nanoscale doping methods for achieving high power properties. (2) Exploring novel electrode and electrolyte materials remains highly desirable, particularly for green Na-ion BSHs. It is an enormous challenge to fabricate high-energy-density Na-ion BSH devices with a high power density. To overcome this, experimental and various computational approaches, such as theory, modeling, and simulations, are required. The aforementioned computational approaches could direct the design options for electrode and electrolyte materials.

FUTURE OUTLOOK

Here, we have discussed recent progress in designing high-performance supercapacitors, such as symmetric and asymmetric supercapacitors, and BSHs. These discussions highlighted several ways to increase the capacitance/working voltage of supercapacitors to address the present shortage of low energy densities. Future trends are listed in the following. Firstly, fully exploring novel types of electrodes and electrolyte materials is still essential regardless of the supercapacitor type. To achieve this, diverse experimental and computational investigations are required, such as theory, modeling, and simulations. Such computational research can direct the design options for electrode and electrolyte materials.

Achieving high-energy-density symmetric supercapacitors (EDLCs) presently remains a major challenge [70–72]. Future work should focus on the increasing capacitance and working voltage by increasing the specific capacitance by enhancing the effective specific surface area, optimizing the pore size and volume, and providing surface functional groups to increase the pseudocapacitance contribution. Moreover, employing various ILs, in which voltage can reach more than 3.0 V, can significantly increase the energy density. Moreover, the synergetic effect of diverse factors is a promising breakthrough trend. However, it remains a tremendous challenge to fully understand the interaction between the pores and electrolyte ions. Considering progress, *in situ* measurement experiments coupled with modeling/simu-

lation will help determine the corresponding mechanism, which may enable the prediction of the optimal surface area, pore size, and electrolyte for maximal energy density.

The clear advantage of ASCs is the wide working voltage window, which significantly increases the energy density. In addition, integrating the various capacitive materials in the form of composites should be further studied to obtain higher energy densities. In future work, significant efforts are required to develop an in-depth understanding of these synergistic effects for integrating the various capacitive composite materials. Considering these advances, high energy densities and real capacitive properties can be achieved by optimizing parameters such as the components and the mass loading of capacitive composite materials.

BSH devices present a promising energy storage device configuration to achieve a high energy density, which is due to the use of high-capacity battery-type electrodes. However, slow redox reactions prevent the further use of these in high power applications. To overcome this, the major approaches to address this are new designs of various nanostructures that can shorten the ion transport route and nanoscale coatings with conductive species that can enhance the conductivity and steadiness. In addition, future research efforts should also focus on the design of nanoscale doping materials to achieve high power properties of BSHs.

The improvement of the energy density based on the device weight, such as the energy density of the next-generation supercapacitor that is almost 100 W h kg^{-1} , can greatly enhance EVs' mobility. In this case, supercapacitors have enormous potential to challenge or even replace Li-ion batteries in applications such as EVs because of the advantages of long cycling life, improved safety, and greater stability and especially short charging times.

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提高超级电容器能量密度的路线: 进步和展望

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摘要 超级电容器与其他能量存储装置相比具有突出的优势, 例如长循环寿命, 快速的充放电过程以及安全性. 然而, 由于超级电容器仍然面临着能量密度低的问题, 这限制了其广泛应用. 我们简要综述了影响超级电容器能量密度的因素, 讨论了如何通过提高电容和工作电压来改善能量密度. 特别地, 我们总结了最近在高能量密度超级电容器方面的一些令人激动的进展, 并着重分析了其未来发展趋势. 最后我们讨论了多种多样的超级电容器, 并提出了一些关键的设计以获得高能量密度.