TOPICAL REVIEW

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Novel mesoporous electrode materials for symmetric, asymmetric and hybrid supercapacitors

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Abstract

Electrochemical capacitors or supercapacitors have achieved great interest in the recent past due to their potential applications ranging from microelectronic devices to hybrid electric vehicles. Supercapacitors can provide high power densities but their inherently low energy density remains a great challenge. The high-performance supercapacitors utilize large electrode surface area for electrochemical double-layer capacitance and/or pseudocapacitance. To enhance the performance of supercapacitors, various strategies have been adopted such as electrode nanostructuring, hybrid electrode designs using nanocomposite electrodes and hybrid supercapacitor (HSC) configurations. Nanoarchitecturing of electrode-active materials is an effective way of enhancing the performance of supercapacitors as it increases the effective electrode surface area for enhanced electrode/electrolyte interaction. In this review, we focus on the recent developments in the novel electrode materials and various hybrid designs used in supercapacitors for obtaining high specific capacitance and energy density. A family of electrode-active materials including carbon nanomaterials, transition metal-oxides, transition metal-nitrides, transition metal-hydroxides, electronically conducting polymers, and their nanocomposites are discussed in detail. The HSC configurations for attaining enhanced supercapacitor performance as well as strategies to integrate with other microelectronic devices/wearable fabrics are also included.

Keywords: supercapacitors, hybrid supercapacitors, battery-type hybrids, mesoporous carbon, carbon nanotubes, micro-supercapacitor, energy storage devices

(Some figures may appear in colour only in the online journal)

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Introduction

Recent advancements in the field of flexible electronic devices and hybrid electric vehicles necessitate the development of new and modified energy storage devices to power their operation [1–3]. Batteries are well established for fulfilling the energy needs for the electronic devices for the past many decades, but their low power density and cycle life remains a great challenge [4]. On the other hand, electrochemical capacitors or supercapacitors have been developed to tackle the issue of power density, but they suffer from low energy density [5–7]. Recently, considerable research effort has been focused on developing novel supercapacitors that can have both high energy density and power density [8–11]. Moreover, recent progress in the field of flexible and wearable microelectronic devices necessitates small and flexible energy storage devices to power them [12, 13]. Batteries such as lithium-ion batteries are not the ideal candidates for this application due to their safety, environment-friendliness, and cost efficiency. In this scenario, supercapacitors have achieved considerable attention since they can be integrated with flexible and wearable devices as well as with other types of energy conversion devices like solar, wind and fuel cells [14–17]. Advancements in the field of nanoscience technology paved the way to use novel electrode materials and electrolytes for manufacturing high-performance supercapacitors. Recent research proves that supercapacitors are promising energy storage devices that can cater to both high energy and power needs of the electronic devices compared to lithium-ion batteries.

Even though several review papers discuss about the supercapacitor electrodes in general, a comprehensive review focusing on the recent developments of mesoporous materials is lacking. Here we review the recent developments of mesoporous electrode materials used in supercapacitors, both in the pristine and composite form. The review begins with a discussion about the strategies adopted to improve the energy and power density of supercapacitors. Based on this strategy, how mesoporous carbons, carbon nanofibers, carbon nanotubes (CNTs) and transition metal oxides, hydroxides and nitrides and their composites can be utilized to achieve high energy and power densities is discussed next. A section talking about the materials used for hybrid supercapacitors (HSCs) (battery-type) is included to give the reader an idea about the ways to improve the energy density of the devices considerably. Different device designs are provided towards the end of the review to familiarize the reader about the various device geometries possible with the mesoporous electrode materials. A schematic which represents various novel mesoporous electrode materials for symmetric, asymmetric and HSCs and innovative supercapacitor electrode designs including sandwich-type, planar-type, yarn-type, and fiber-type and various applications of supercapacitors are depicted in figure 1. The review concludes with a summary of the mesoporous materials reviewed and the future directions of research.

It is to be noted that devices can be categorized as pseudocapacitors only when the electrodes show an activated carbon (AC)-based electrode appearance, i.e. rectangular cyclic voltammetry curve (similar to electrochemical double layer capacitor (EDLC)). This behavior is clearly shown by a few transition metal-oxide electrode materials like manganese oxide (MnO2) and ruthenium oxide (RuO2) [18]. These electrode materials show a linear dependence of stored charges with changing potential. However, many papers discuss battery-type behavior also as pseudocapacitive electrode performance. To avoid confusion, we follow the same terminology used by authors of a given article to discuss their results, agreeing to the fact that they are not strictly pseudocapacitors.

Energy storage mechanisms

A typical supercapacitor consists of an anode, cathode, an electrolyte, and a separator. A schematic diagram of the structure of the supercapacitor comprising of these components is shown in figure 2(a). An ion porous separator separates anode and cathode. The energy is stored at the interphase of electrode and electrolyte. Generally, there are three types of supercapacitors namely, EDLCs, pseudocapacitors and HSCs [13]. The charge storage mechanism in EDLCs is purely non-faradaic in nature. This means that there is no chemical reaction or charge transfer at the electrode/electrolyte interface during charge–discharge cycles. However, in the case of pseudocapacitors (otherwise known as redox capacitors or ultracapacitors), the charge storage is accomplished by means of faradaic reaction. The electrode-active material undergoes reversible oxidation-reduction processes during the charge–discharge process. The EDLCs and pseudocapacitors are still facing a problem of low energy density. In the case of an EDLC, charge storage occurs at the electrode/electrolyte interface by the formation of an electric double layer with the electrolyte ions on the electrode-active materials. The amount of charges stored will depend on the available surface sites of the active material opened to the electrolyte-ions. The capacitance of a capacitor is calculated from the expression

\[
C = \frac{A\varepsilon_0}{d},
\]

where \(C\), \(A\), \(\varepsilon_0\), and \(d\) are the capacitance, electrode area, dielectric constant of free space, and dielectric thickness, respectively. The requirements of electrode-active materials are high electrochemical stability and larger accessible surface area. The capacitance of a supercapacitor depends mainly on the electrolyte accessible surface area of the electrode-active material. This, in turn, depends on the porosity as well as the pore-size of electrodes since this will allow the easy movement of the electrolyte-ions through it. Mesoporous materials (those have pore-size between 2 and 50 nm) are preferred since their double layer capacitance is very high. A good example for a mesoporous electrode material which exhibits double layer capacitance is mesoporous carbon. The unique properties such as natural abundance, low cost, good electronic conductivity, sustainability, good chemical, electrochemical and thermal resistance, light-in-weight, etc have
attracted them to use as electrode materials in EDLCs. The large surface area and open pore structure helped them to obtain high specific capacitances and energy densities. The tunability in the pore size and pore-size distribution while adopting different processing conditions have made them unique materials as EDLC electrodes. Long cycle life with capacitance retention is another merit of mesoporous carbon electrodes which enables the EDLC to work for thousands of cycles without any deterioration in its performance hence it is a very important electrode material [19]. Due to these various reasons, mesoporous carbons are invariably used in current commercial supercapacitors. In an EDLC, the adsorption/desorption of the electrolyte-ions on the electrode surface takes place during the charge/discharge process (figure 2(b)). In a pseudocapacitor, the electrode-active material undergoes reduction-oxidation processes (figure 2(c)). Not only the electrode-active materials but also the electrolyte plays a significant role in determining the operating potential window of the supercapacitors. The low operation voltage of aqueous electrolytes has led to the wide acceptance of organic electrolytes and ionic liquids. The energy stored in a supercapacitor is given by the expression

\[ E = \frac{CV^2}{2}, \]

where \( C \) is the capacitance of the supercapacitor and \( V \) is the voltage, means the energy stored in a supercapacitor depends on the operating voltage (voltage window within which there is no electrolyte decomposition). Generally, the energy density of an EDLC is limited due to their non-faradaic charge storage, but it is comparatively high for pseudocapacitors. The energy density of supercapacitors lies in the range of minimum values reported for the existing thin film lithium-ion (Li-ion) batteries. To fulfill the needs of a variety of electronic devices, supercapacitors should provide both high power and energy densities.

**Strategies for high-performance supercapacitors**

Zero-dimensional, one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanostructures are invariably used for enhancing the effective surface area of the supercapacitor electrodes [20–22]. Large surface area providing electronically conducting carbon nanomaterials have achieved great interest in the recent past [23–27]. Carbon nanomaterials including activated porous carbons, carbon nanofibers (CNFs), CNTs, carbon nanopetals, graphene, graphene-oxide, exfoliated-graphite nanosheets, etc exhibit excellent chemical and electrochemical stabilities and are used as electrode materials for supercapacitors with long cycle life and shelf-life [28–32]. Most of the carbon nanomaterials exhibit electric double layer formation for their charge storage; e.g. mesoporous carbons, CNFs and CNTs. However, in the case of graphene-oxide and reduced
graphene-oxide, the charge storage is due to both electric double layer and faradaic reaction. Among the family of carbon nanomaterials, CNFs, CNTs and graphene have achieved great attention due to their unique features such as a large surface area to volume ratio, good electronic conductivity, excellent stability, etc. In addition, they are found to be useful in manufacturing various nanocomposites since they can form entangled network during their preparation to improve the electrode conductivity [33]. The technological advancements in the field of nanoscience helped the developments of high power EDLCs, but the lack of energy density remains a big challenge. Other promising electrode candidates for supercapacitors include various oxides, nitrides, and hydroxides of transition metals. They exhibit good redox behaviors, hence are widely used as supercapacitor electrode materials. Most of these materials are of low cost and thus feasible for commercialization.

Electronically conducting polymers such as polythiophenes (PTHs), polypyrrole (PPY), polyaniline (PANI), etc have emerged as novel supercapacitor electrode materials due to their unique features such as low density, good electronic conductivity, good electrochemical properties, etc [34–36]. Various nanostructures of electronically conducting polymers are invariably used in different forms such as thin films, powders, nanotubes etc for supercapacitor electrode fabrication. Apart from the nanostructuring of the electrode-active materials, another approach for improving the supercapacitor performance is to use nanocomposite electrodes using various electrode-active materials. The advantage of this approach is that the individual benefits of the electrode-active materials can be achieved in the nanocomposites as well as their demerits can be minimized. Supercapacitor electrodes are made by compositing two or more electrode-active materials. Flexible supercapacitor electrodes can be prepared by compositing electronically conducting polymers with other electrode-active materials such as carbon nanomaterials, transition metal-oxides, transition metal-nitrides, etc. By using such flexible electrodes, flexible and wearable supercapacitors can be developed which is mandatory for powering the futuristic flexible and wearable electronic devices. Examples for the nanocomposite electrodes used in supercapacitors are carbon/carbon nanocomposites, carbon nanomaterial/electronically conducting polymer nanocomposites, carbon nanomaterial/transition metal-oxide nanocomposites, transition metal-nitride/carbon nanomaterial nanocomposites, etc [5, 37–44].

Figure 2. Schematic representation of (a) the structure of a supercapacitor, (b) electrochemical double layer formation, and (c) faradaic reactions at the electrodes.
Mesoporous electrode materials

To a large extent, the electrode-active materials determine the electrochemical performance of a supercapacitor. The electrode/electrolyte interfacial reactions lead to the charge storage in supercapacitors whether it is a faradaic-type or non-faradaic type of reactions. Equal importance should be given to the selection of electrolytes as it determines the operating voltage window of the supercapacitor. Electrode nano-structuring, hybrid electrode designs using nanocomposite electrodes and HSC configurations are some of the strategies adopted in the recent past for obtaining both high energy and power densities in supercapacitors [45–52]. To achieve this, novel electrode materials and hybrid electrode designs have been developed. Nanostructuring of electrode-active materials is one of the strategies used in the recent past and is an effective way of enhancing the performance of supercapacitors as it increases the effective electrode surface area for enhanced electrode/electrolyte interaction.

Mesoporous carbons

Mesoporous carbon nanomaterials were utilized for a variety of applications like electrodes, catalyst supports, and water purification in the past [53, 54]. Usually, non-activated porous carbons show feeble electrochemical properties and hence activation is an important step before their use in supercapacitors. Synthesis of carbon nanomaterials with mesoporous structure is mandatory to obtain the best performance for the supercapacitor. Mesoporous carbons with pore-size between 2 and 4 nm can be obtained by the pyrolysis of a block copolymer, polyacrylonitrile-b-polystyrene-b-polyacrylonitrile [55]. The supercapacitor assembled using these mesoporous carbon electrodes exhibited a capacitance of 185 F g$^{-1}$ at a current density of 0.625 A g$^{-1}$ in 2 M aqueous potassium hydroxide (KOH) electrolyte. Li et al have synthesized mesoporous carbons enriched with nitrogen via solvent evaporation induced self-assembly method for supercapacitor application [56]. The nitrogen-doped mesoporous carbons possessed a large Brunauer–Emmett–Teller (BET) surface area of 2828.8 m$^{2}$ g$^{-1}$ whereas it was 1244.6 m$^{2}$ g$^{-1}$ for the mesoporous carbon without nitrogen content. The nitrogen-doped mesoporous carbon electrodes-based supercapacitor displayed a specific capacitance of 388 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$ with good cycling stability of over 5000 cycles. Pore structure and shape of mesoporous carbons can be tailored by using hard templates like colloidal silica crystals and porous silica [57]. Not only silica templates, but other novel templates can also be used for the synthesis of mesoporous carbons, for example, carbon nitride (g-$\text{C}_3\text{N}_4$) template. A novel approach utilizing the g-$\text{C}_3\text{N}_4$ template to synthesize nitrogen-rich porous graphene-like carbon sheets (NPGCs) by plasma enhanced chemical vapor deposition (CVD) method is reported in the recent past [58]. The morphological characteristics including scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive x-ray spectroscopy of the as-synthesized NPGCs showed that they exhibit large surface area of 1277 m$^{2}$ g$^{-1}$ with a nitrogen content of 8.75 wt%. The supercapacitor fabricated using NPGCs electrodes displayed a specific capacitance of 261 F g$^{-1}$ at a current density of 1 A g$^{-1}$ and 189 F g$^{-1}$ at a high current density of 100 A g$^{-1}$, which shows that it exhibits good rate capability. The NPGCs supercapacitor possessed an energy density of 6.53 W h kg$^{-1}$ with a power density of 28.4 kW kg$^{-1}$.

Yang et al have synthesized mesoporous carbons doped with nitrogen using silica gel template via sol–gel process [59]. The importance of this method is that the porosity of carbons can be tuned by varying the concentrations of the precursor solutions and the as-synthesized porous carbons possessed a maximum BET surface area of 663 m$^{2}$ g$^{-1}$. The percentage of mesopore volume to the total pore volume of the porous carbons was 96.68%. These carbons were used for assembling a supercapacitor which displayed a specific capacitance of 190 F g$^{-1}$. Li et al have synthesized mesoporous carbons with uniform pore-size using a post-treatment-free synthesis method [60]. This method helps in avoiding the post-treatment steps for removing the silica template by a hazardous chemical like hydrofluoric acid or sodium hydroxide. The as-obtained disordered mesoporous carbons possessed a BET surface area of 2302 m$^{2}$ g$^{-1}$. The mesopores to total pores ratio was 99.6%. A supercapacitor fabricated using these disordered carbon electrodes displayed a specific capacitance of 201 F g$^{-1}$ with a high energy density of 28.3 W h kg$^{-1}$. To improve the performance of supercapacitors, an increased electrode surface area is mandatory. To accomplish this, an easy synthesis method for producing mesoporous carbon with a tubular structure via a nanocasting process is reported [61]. The template material used was SBA-15 with furfuryl alcohol as the carbon source, and oxalic acid played the role of a catalyst during the nanocasting process. This method enabled in obtaining a large BET surface area of 2500 m$^{2}$ g$^{-1}$ for the as-synthesized tubular mesoporous carbon structures. Mesoporous carbons with controlled morphologies such as films, powders and nanofibers can be synthesized by an organic–organic interaction, which includes a dual-templating approach using a hard template of anodic aluminum oxide [62]. Highly ordered mesoporous carbons (OMCs) architectures can be synthesized using Pluronic F127 as the template and phenolic resol as the carbon precursor and it is a versatile method for the largescale manufacturing of the same [63]. The OMC exhibited a maximum BET surface area of 690 m$^{2}$ g$^{-1}$ with a large pore volume of 0.45 cm$^{3}$ g$^{-1}$. The percentage of BET surface area was attributed from the mesopores, which is calculated to be 50%. A supercapacitor assembled using these OMCs-based electrodes tested in 6 M KOH electrolyte exhibited a specific capacitance of 130 F g$^{-1}$.

Highly porous carbons can be synthesized from polyaniline base by potassium carbonate activation [64]. The as-synthesized activated porous carbon electrodes exhibit good electrochemical behaviors with a specific capacitance of 210 F g$^{-1}$. Nanoporous carbon membranes were synthesized by pyrolysis of polymeric composite films with a cross-linker hexamethylenetramine and achieved a uniform pore-size of 6.4 nm with a precise control in the wall thickness [65]. A
Different strategies are used to synthesize CNFs such as electrode materials in EDLCs due to their unique properties [66]. This method avoids any pre-and post-synthesis treatments for obtaining mesoporosity in the carbon. A simple and cost-effective method for synthesizing ACs is carbonizing the coconut shell. The BET surface area of the as synthesized AC can be as high as 2000–2500 m² g⁻¹ [67]. A two-step process is involved in the synthesis, carbonization process of the coconut shell and an activation process. Green energy approach for synthesizing mesoporous carbon materials for supercapacitor application is booming now-a-days due to its natural abundance, safety, and environment-friendliness. Fu et al. have synthesized porous carbons from crab shell as the carbon precursor by a simple procedure involving carbonization, acid treatment and followed by activation at different temperatures [24]. The supercapacitors assembled using A-C-CS600, A-C-CS700 and A-C-CS800 electrodes exhibited good electrochemical performance with A-C-CS700 exhibiting a high specific capacitance of 341.4 F g⁻¹ and excellent cycling stability of 99% even after 10,000 cycles.

Mesoporous carbons synthesized by a self-templating process possessed a BET surface area of 2012 m² g⁻¹ with pore-size ranging from 2 to 50 nm [68]. The supercapacitor fabricated using these mesoporous carbon electrodes exhibited a specific capacitance of 259 and 189 F g⁻¹ at a current density of 1 and 100 A g⁻¹, respectively. The capacitance retention indicates that the electrodes possess good rate capability. Hetero-atom doped mesoporous carbons are potential candidates for supercapacitor electrode application since they exhibit high specific capacitance which arises from the faradic reactions [69]. Brandiele et al. have synthesized mesoporous carbons doped with nitrogen and sulfur by templating silica and used as electrode materials in supercapacitors [70]. The symmetric supercapacitor assembled using nitrogen-doped mesoporous carbon electrodes displayed a gravimetric capacitance of 170 F g⁻¹ with an areal capacitance of 835 F m⁻². Nitrogen-doped ordered mesoporous carbon (N-OMC) synthesized by solid-solid grinding found to have a large specific surface area of 1006 m² g⁻¹ with a pore volume of 0.96 cm³ g⁻¹ with a pore size of 3.6 nm [71]. The mesopores were formed by the removal of SBA-15 template used in the synthesis process. The N-OMC based supercapacitor electrode displayed a specific capacitance of 228 F g⁻¹ at a current density of 0.2 A g⁻¹.

Carbon nanofibers

The CNFs are 1D carbon nanostructures used widely as electrode materials in EDLCs due to their unique properties such as easy processability, light-in-weight, large surface area, mesoporous architecture, good chemical and electrochemical stabilities, etc. The long cycling stability is an added advantage of CNFs based supercapacitor electrodes [72–74]. Different strategies are used to synthesize CNFs such as CNFs derived from polymer blends, use of sacrificial polymers in the carbon fiber (CF), use of degradable small molecules in CNFs, etc [75–77]. The mesoporous CNFs synthesized by carbonization followed by CO₂ activation from polymer blends comprising of polyacrylonitrile (PAN) and polymethylmethacrylate (PMMA) exhibited a high surface area of 2419 m² g⁻¹ in which the as synthesized fibers possess high degree of graphitization for PAN:PMMA ratio of 95:5 [76]. The total pore volume of the CNFs was 1.3128 cm³ g⁻¹ out of which the mesopore volume was 0.6744 cm³ g⁻¹ (mesopore percentage of 51.37%). These CNFs exhibited a specific capacitance of 140 F g⁻¹ with an energy density of 101 Wh kg⁻¹ in an ionic electrolyte. The mesoporous CNFs synthesized by confined self-assembly of triblock copolymers exhibited a BET surface area of 1424 m² g⁻¹ [78]. The mesoporous channels arranged concentrically around the longitudinal axis helps in shortening of the diffusion distance to the electrolyte ions to migrate thereby achieved a specific capacitance of 152 F g⁻¹ at a scan rate of 5 mV s⁻¹. Mesoporous ribbon shaped graphitic CNFs (MRCNFs) with pore size ranging from 2 to 10 nm were used as supercapacitor electrodes, recently [79]. The MRCNFs were synthesized by a procedure combining electrospinning, templating and catalytic graphitization and the BET surface area of the obtained MRCNFs was 463 m² g⁻¹ with a total pore volume of 0.575 cm³ g⁻¹ out of which the mesopore volume was 0.482 cm³ g⁻¹. The percentage of mesopore volume to the total pore volume of the MRCNFs was 84%. The supercapacitor electrodes exhibited a specific capacitance of 228 F g⁻¹ at a current density of 0.2 A g⁻¹. The graphitic CNFs electrodes possessed good capacitance retention of 95% after 5000 cycles. A novel strategy of combining micro-/mesoporous CNFs embedded in an ordered carbon to synthesize flexible supercapacitor electrodes was reported in the recent past [80]. The CNFs thus synthesized were having surface area of 533 m² g⁻¹ with an average pore diameter of 3.28 nm. The microporous and mesoporous volume of the CNFs were 0.24 and 0.35 cm³ g⁻¹, respectively. The flexible supercapacitor assembled using these CNFs exhibited a specific capacitance of 272.7 F g⁻¹. Mesoporous CNFs synthesized by electrospinning resol resin where F127 was used to form Mesopores [81]. The electrospinning step was followed by carbonization and pickling procedures to obtain mesoporous CNFs and they possessed a BET surface area of 1674 m² g⁻¹ with a mesoporous volume of 0.906 cm³ g⁻¹. The percentage of mesopore volume to the total pore volume of the mesoporous CNFs was 64%. The microporous CNFs were turned to mesoporous CNFs after the F127 is added to the electrospinning solution. The CNF electrodes showed a specific capacitance of 210 F g⁻¹ at a current density of 0.5 A g⁻¹ with a capacitance retention of 71% when cycled at a higher current density of 30 A g⁻¹. A novel self-template strategy involving a solution growth pathway to synthesize mesoporous CNFs was reported [82]. Initially, zinc oxide (ZnO)/carbon core/shell nanostructure was constructed with a shell thickness of 30 nm and it was further etched completely in order to obtain the whole fiber. The morphology of the mesoporous CNFs is shown in figures 3(a)–(f). The surface of the CNFs was having mesopores with diameters ranging from 10 to 20 nm. The CNFs synthesized by this
method possessed a 3D interconnected mesoporous network favored superior charge storage due to minimized inner pore resistance. These CNFs possessed a BET surface area of 1725 m² g⁻¹ and bimodal pores observed with sizes 1.1 and 3.4 nm. The percentage of mesopore volume to the total pore volume of the mesoporous CNFs was 81.48%. The ZnO acted here as an in situ porogen. The mesoporous CNFs exhibited a specific capacitance of 280 F g⁻¹ at 0.5 A g⁻¹. The superior performance was attributed to the presence of surface oxygen functional groups which favored pseudocapacitance. Mesoporous CNFs with 59% of mesopores was used to construct a symmetric supercapacitor [83]. The symmetric supercapacitor assembled has displayed a specific capacitance of 52 F g⁻¹ with a specific power of 1.8 kW kg⁻¹ at a scan rate of 5 mV s⁻¹ in 6 M aqueous KOH electrolyte.

Doping hetero-atoms within the CNFs were accepted as a novel strategy for improving the electrochemical performance of CNF electrodes for supercapacitor applications [84, 85]. In situ nitrogen-doped CNFs were synthesized by electrospinning followed by carbonization and etching procedures [86]. Here, Mg(OH)₂ acted as an in situ porogen as well as a structural constructor. The BET surface area of the nitrogen-doped CNFs was 926.4 m² g⁻¹ with pore volume of 0.42 cm³ g⁻¹ and the average pore diameter was 4.26 nm. These free-standing CNFs electrodes-based supercapacitor cell delivered excellent electrochemical performances bearing a specific capacitance of 327.3 F g⁻¹ at 1 A g⁻¹ in 6 M aqueous KOH electrolyte with a capacitance retention of 93% even after 10,000 cycles when cycled at a current density of 20 A g⁻¹. Nitrogen-doped mesoporous CNFs synthesized by carbonizing the macroscopic scale CNFs deposited with PPY at an annealing temperature of 900 °C [87]. The morphologies of macroscopic scale CNFs, PPY-coated CNFs and nitrogen-doped CNFs are depicted in figure 4. The macroscopic scale CNFs exhibited a BET surface area of 348.12 m² g⁻¹ (with an average pore diameter of 5.07 nm) whereas the nitrogen-doped CNFs possessed a surface area of 562.51 m² g⁻¹ (with an average pore diameter of 3.64 nm). The nitrogen-doped CNFs electrode delivered a specific capacitance of 202 F g⁻¹ with a high power density of 89.57 kW kg⁻¹ at a current density of 1 A g⁻¹ along with good rate capability.

Carbon nanotubes

The CNTs are another class of promising candidates in the family of carbon nanomaterials. The CNTs are 1D carbon nanostructures with good electronic conductivity and large surface area to volume ratio [88–94]. Both single-walled CNTs and multi-walled CNTs (MWCNTs) are invariably used as electrode-active materials in supercapacitors due to their high specific capacitance and long cycling stability. They are also used for making nanocomposites with a variety of other electrode-active materials [95–98]. Their entanglement in the nanocomposites helps in enhancing the supercapacitor performance as the charge transfer between the filler components will be easy and the transport of electrons through the 1D CNTs are very fast. Zhou et al have synthesized a novel CNT/graphite nanofiber nanocomposite by CVD method [99]. The schematic of CNTs/graphite nanofibers architecture is depicted in figure 5(a) and a symmetric supercapacitor was fabricated using CNTs/graphite nanofibers electrodes (figure 5(b)). The morphology of CNTs/graphite nanofibers electrodes was bird
nest-type (figures 5(c)–(f)) and exhibit a large surface area of 1863.1 m² g⁻¹. The CNTs/graphite nanofibers supercapacitor displayed a maximum specific capacitance of 270 F g⁻¹ with an energy density of 72.2 Wh kg⁻¹ and a power density of 686 W kg⁻¹ at a current density of 1 A g⁻¹ in 6 M KOH electrolyte. When increased the current density to 10 A g⁻¹, the capacitance dropped down to 221 F g⁻¹. It exhibited good capacitance retention of 96% after cycled to 10 000 cycles.

Depositing CNTs on flexible substrates is beneficial for manufacturing flexible electrodes for supercapacitors, and such flexible capacitors are in high demand for applications in flexible and wearable electronic devices. The CNTs grown on nickel nanoparticles-coated unidirectional CF (SEM images shown in figure 6) are found to be an effective way of utilizing the surface area of CNTs without destroying the porous architecture of the electrode [100]. The vertically aligned
CNTs synthesized on nickel nanoparticles-coated CFs possessed a BET surface area of 553.8 m$^2$/g$^{-1}$. The symmetric supercapacitor assembled using CNTs grown on CFs functioning as both electrode and current collector (back electrode) exhibit a high volumetric capacitance of 3.4 F cm$^{-3}$ and a power density of 1195 mW cm$^{-3}$ in 5 M aqueous KOH electrolyte. Long cycle life of more than 27,000 cycles can be attained for the CNT supercapacitor. This is an attractive approach to make supercapacitors with high cycle life.

Not only vertically aligned CNTs, helically coiled CNTs have also found application as supercapacitor electrodes. The helically coiled CNTs grown on CFs were synthesized by CVD method using thiophene as an impurity donor [101]. A symmetric supercapacitor was assembled using helically coiled CNTs as electrodes and exhibited a gravimetric capacitance of 125.7 F g$^{-1}$ at a current density of 0.28 mA cm$^{-2}$. The CNTs are the best filler materials in the preparation of electronically conducting polymer-based nanocomposites for the fabrication of flexible supercapacitors. The formation of the entangled network of CNTs within the electronically conducting polymer network helps in enhancing the electronic conductivity of the nanocomposite. It also improves the redox performance of the conducting polymers. Wu et al have prepared CNT/PANI nanocomposites by electrochemical induction at 0.75 V [102]. The supercapacitor assembled using CNT/PANI nanocomposites electrodes displayed a specific capacitance of 403.3 F g$^{-1}$ in perchloric acid and 314.6 F g$^{-1}$ in 1-Ethyl-3-methylimidazolium tetrafluoroborate (a room temperature ionic liquid) electrolyte. The supercapacitor retained 90.2% of its capacitance after 3000 cycles when cycled at a current density of 4 A g$^{-1}$. The CNT/PPY nanocomposite electrodes prepared by electrochemical deposition method was used for the fabrication of a flexible symmetric supercapacitor which exhibited capacitance of 305 F g$^{-1}$ with an energy density of 42 Wh kg$^{-1}$ [103]. The CNT/PPY supercapacitor also showed a high-volume specific capacitance of 14,950 mF cm$^{-3}$ at a current density of 2.5 mA cm$^{-2}$. A table comprising the characteristics of mesoporous carbons-based supercapacitor electrodes in terms of synthesis method, surface area, pore-size, active-mass loading, specific capacitance, rate capability, and cycling stability is given in table 1.

### Transition metal-oxides, hydroxides and nitrides

Carbon nanomaterials are well established for supercapacitor electrode application, yet they suffer from low specific capacitance. This has motivated researchers to explore other potential electrode materials like transition metal-oxides, hydroxides and nitrides as possible candidates for energy storage applications. These materials exhibit good chemical and electrochemical stabilities, environmental-friendliness and high theoretical capacitance. The most commonly used electrode materials include oxides, hydroxides, and nitrides of ruthenium (Ru), manganese (Mn), nickel (Ni), iron (Fe), cobalt (Co), vanadium (V), etc [104–114]. Despite providing large surface area and theoretical capacitance, these materials still suffer from poor electrical conductivity which leads to low power density. This can be avoided by preparing nanocomposite electrodes.
<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesis method</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore size (nm)</th>
<th>Active mass loading (mg)</th>
<th>Specific capacitance</th>
<th>Rate capability</th>
<th>Cycle stability (retention %)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous carbons</td>
<td>Pyrolysis of polymers</td>
<td>953.53</td>
<td>2–4</td>
<td>—</td>
<td>185 F g⁻¹ at 0.1 A g⁻¹</td>
<td>67.5% at 6.25 A g⁻¹</td>
<td>97.5% after 10,000 cycles</td>
<td>[55]</td>
</tr>
<tr>
<td>Nitrogen-doped mesoporous carbon</td>
<td>Solvent evaporation induced self-assembly</td>
<td>2828.8</td>
<td>4</td>
<td>1.5–3</td>
<td>388 F g⁻¹ at 0.5 A g⁻¹</td>
<td>70% at 50 A g⁻¹</td>
<td>100% after 5000 cycles</td>
<td>[56]</td>
</tr>
<tr>
<td>Nitrogen rich porous graphene-like carbon sheets</td>
<td>Hard template</td>
<td>1277</td>
<td>2–30</td>
<td>1.1</td>
<td>261 F g⁻¹ at 1 A g⁻¹</td>
<td>72% at 100 A g⁻¹</td>
<td>97% after 20,000 cycles</td>
<td>[58]</td>
</tr>
<tr>
<td>Nitrogen doped mesoporous carbon</td>
<td>Sol–gel</td>
<td>663</td>
<td>30</td>
<td>1.6–4</td>
<td>190 F g⁻¹ at 0.1 A g⁻¹</td>
<td>80% at 20 A g⁻¹</td>
<td>99% after 5000 cycles</td>
<td>[59]</td>
</tr>
<tr>
<td>Mesoporous carbon</td>
<td>Sol–gel + carbonization</td>
<td>2302</td>
<td>4.9</td>
<td>—</td>
<td>201 F g⁻¹ at 0.02 A g⁻¹</td>
<td>49% at 50 A g⁻¹</td>
<td>—</td>
<td>[60]</td>
</tr>
<tr>
<td>Highly ordered mesoporous carbon</td>
<td>Template method</td>
<td>690</td>
<td>4.5</td>
<td>—</td>
<td>130 F g⁻¹ at 0.5 A g⁻¹</td>
<td>69% at 15 A g⁻¹</td>
<td>—</td>
<td>[63]</td>
</tr>
<tr>
<td>Highly porous carbon</td>
<td>Potassium carbonate activation</td>
<td>917</td>
<td>1.39</td>
<td>—</td>
<td>210 F g⁻¹ at 2 mVs⁻¹</td>
<td>86.7% at 20 mVs⁻¹</td>
<td>—</td>
<td>[64]</td>
</tr>
<tr>
<td>Mesoporous carbon</td>
<td>Self-templating method</td>
<td>2012</td>
<td>4–5</td>
<td>—</td>
<td>259 F g⁻¹ at 1 A g⁻¹</td>
<td>73% at 100 A g⁻¹</td>
<td>92% after 6000 cycles</td>
<td>[68]</td>
</tr>
<tr>
<td>Nitrogen- doped mesoporous carbon</td>
<td>Template method</td>
<td>200</td>
<td>13–14</td>
<td>—</td>
<td>167 F g⁻¹ at 0.5 mVs⁻¹</td>
<td>—</td>
<td>100% after 1000 cycles</td>
<td>[70]</td>
</tr>
<tr>
<td>Micro-/mesoporous CNFs</td>
<td>Coaxial electrospinning</td>
<td>533</td>
<td>3.28</td>
<td>—</td>
<td>272.7 F g⁻¹ at 1 A g⁻¹</td>
<td>15.9 F g⁻¹ at 10 A g⁻¹</td>
<td>96.7% after 3000 cycles</td>
<td>[80]</td>
</tr>
<tr>
<td>Ribbon-shaped graphitic CNFs</td>
<td>Electrospinning + templating + catalysis</td>
<td>463</td>
<td>2–10</td>
<td>1.5</td>
<td>228 F g⁻¹ at 0.2 A g⁻¹</td>
<td>58% at 20 A g⁻¹</td>
<td>95% after 5000 cycles</td>
<td>[79]</td>
</tr>
<tr>
<td>Mesoporous CNFs</td>
<td>Electrospinning</td>
<td>1674</td>
<td>—</td>
<td>—</td>
<td>210 F g⁻¹ at 0.5 A g⁻¹</td>
<td>71% at 30 A g⁻¹</td>
<td>—</td>
<td>[81]</td>
</tr>
<tr>
<td>Mesoporous CNFs</td>
<td>Solution growth</td>
<td>1725</td>
<td>1.1</td>
<td>3.4</td>
<td>280 F g⁻¹ at 0.5 A g⁻¹</td>
<td>71.43 at 5 A g⁻¹</td>
<td>91% after 1000 cycles</td>
<td>[82]</td>
</tr>
<tr>
<td>Mesoporous CNFs</td>
<td>Self-assembly</td>
<td>1424</td>
<td>5–8</td>
<td>—</td>
<td>152 F g⁻¹ at 3 mVs⁻¹</td>
<td>—</td>
<td>100% after 1000 cycles</td>
<td>[78]</td>
</tr>
<tr>
<td>Nitrogen-doped CNFs</td>
<td>Electrospinning</td>
<td>926.4</td>
<td>4.26</td>
<td>—</td>
<td>327.3 F g⁻¹ at 1 A g⁻¹</td>
<td>93% at 20 A g⁻¹</td>
<td>93% after 10,000 cycles</td>
<td>[86]</td>
</tr>
<tr>
<td>Nitrogen-doped CNFs</td>
<td>Carbonization</td>
<td>562.51</td>
<td>3.64</td>
<td>3.4</td>
<td>202 F g⁻¹ at 1 A g⁻¹</td>
<td>81.72% at 30 A g⁻¹</td>
<td>97% after 3000 cycles</td>
<td>[87]</td>
</tr>
<tr>
<td>rGO/MWCNT microspheres</td>
<td>Spray drying</td>
<td>—</td>
<td>—</td>
<td>3</td>
<td>293 mF cm⁻² at 0.2 A g⁻¹</td>
<td>46% at 100 A g⁻¹</td>
<td>98% after 5000 cycles</td>
<td>[94]</td>
</tr>
<tr>
<td>Vanadium nitride nanowire arrays on CNTs</td>
<td>Hydrothermal + annealing</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>715 mF cm⁻² at 1 mA cm⁻²</td>
<td>68.8% at 10 mA cm⁻²</td>
<td>90% after 10,000 cycles</td>
<td>[95]</td>
</tr>
<tr>
<td>MnO₂-CNT</td>
<td>Wet chemical synthesis</td>
<td>202</td>
<td>15.3</td>
<td>6.4</td>
<td>1 F cm⁻² at 1.28 mA cm⁻²</td>
<td>77% at 128 mA cm⁻²</td>
<td>84.5% after 3000 cycles</td>
<td>[96]</td>
</tr>
<tr>
<td>Material</td>
<td>Synthesis method</td>
<td>Surface area (m² g⁻¹)</td>
<td>Pore size (nm)</td>
<td>Active mass loading (mg)</td>
<td>Specific capacitance</td>
<td>Rate capability</td>
<td>Cycle stability (retention %)</td>
<td>References</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------------------------------------</td>
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<td>--------------------------</td>
<td>----------------------</td>
<td>----------------</td>
<td>-------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Ni(OH)₂-graphene sheet-CNT composite</td>
<td>Solvothermal + chemical precipitation</td>
<td>272.89</td>
<td>4.92</td>
<td>8</td>
<td>1170.38 F g⁻¹ at 0.2 A g⁻¹</td>
<td>73.04% at 1.2 A g⁻¹</td>
<td>80% after 1000 cycles</td>
<td>[97]</td>
</tr>
<tr>
<td>α-Fe₂O₃/CNTs</td>
<td>CVD + hydrothermal</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>296.3 F g⁻¹ at 5 mV s⁻¹</td>
<td>34% at 300 mV s⁻¹</td>
<td>60% after 1000 cycles</td>
<td>[98]</td>
</tr>
<tr>
<td>CNT/graphite nanofiber nanocomposite</td>
<td>CVD</td>
<td>1863.1</td>
<td>2–5</td>
<td>—</td>
<td>270 F g⁻¹ at 1 A g⁻¹</td>
<td>82% at 10 A g⁻¹</td>
<td>—</td>
<td>[99]</td>
</tr>
<tr>
<td>Vertically aligned CNTs grown on unidirectional carbon fiber</td>
<td>CVD</td>
<td>553.8</td>
<td>8</td>
<td>—</td>
<td>3.4 F cm⁻³</td>
<td>—</td>
<td>60% after 27 000 cycles</td>
<td>[100]</td>
</tr>
<tr>
<td>Helically coiled CNTs grown on unidirectional carbon fiber</td>
<td>CVD</td>
<td>286.5</td>
<td>3.8</td>
<td>—</td>
<td>125.7 F g⁻¹ at 0.28 mA cm⁻²</td>
<td>40% at 8.33 mA cm⁻²</td>
<td>100% after 15 000 cycles</td>
<td>[101]</td>
</tr>
<tr>
<td>PANI/VA-CNTs nanocomposite</td>
<td>Electrochemical induction + electrochemical polymerization</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>403.3 F g⁻¹ at 1 A g⁻¹</td>
<td>68% at 20</td>
<td>90.2% after 3000 cycles</td>
<td>[102]</td>
</tr>
<tr>
<td>CNT/PPY nanocomposite</td>
<td>Electrochemical deposition</td>
<td>218</td>
<td>13</td>
<td>—</td>
<td>305 F g⁻¹ at 2.5 mA cm⁻²</td>
<td>26% at 7.5 mA cm⁻²</td>
<td>100% after 5000 cycles</td>
<td>[103]</td>
</tr>
</tbody>
</table>
An interesting direction to make a composite electrode is to grow amorphous MnO\textsubscript{2} nanoparticles uniformly over MWCNT fiber. The uniform deposition of MnO\textsubscript{2} and close contact with the fibers help in achieving high surface and better charge–discharge capabilities. A solid-state supercapacitor prepared with these composite fibers were able to achieve a volumetric capacitance of 8 F cm\textsuperscript{-3} and retaining 90\% of its capacitance after 15 000 cycles [115]. The surface area can be increased by converting the existing nanosstructures porous and this helps in achieving specific capacitance value close to its theoretical value without using any conducting additive. Mesoporous manganese oxide nanocoons (MONCs) developed via safe over-reduction annealing treatment without toxic reagents provided a high surface area of 379.7 m\textsuperscript{2} g\textsuperscript{-1} [116]. Asymmetric supercapacitor fabricated with MONCs as cathode and AC as anode delivered a maximum energy density of 32 Wh kg\textsuperscript{-1} at a power density of 185 W kg\textsuperscript{-1} with a cycle life of 5000 cycles (with ~98\% capacitance retention). Cobalt oxide (Co\textsubscript{3}O\textsubscript{4}), another pseudocapacitive material with high theoretical capacitance has been explored in the recent past as a promising supercapacitor electrode. Subramani \textit{et al} have developed a nanocomposite consisting of Co\textsubscript{3}O\textsubscript{4} and reduced graphene oxide (rGO) via chemical co-precipitation method [117]. This nanocomposite provided a specific capacitance of 784 F g\textsuperscript{-1} at a current density of 1 A g\textsuperscript{-1} in KOH electrolyte. An asymmetric supercapacitor fabricated with rGO delivered 245 F g\textsuperscript{-1} at 0.5 A g\textsuperscript{-1} with high energy and power densities of 16.6 Wh kg\textsuperscript{-1} and 3473 W kg\textsuperscript{-1}, respectively. A pouch cell prepared was able to retain 94\% capacitance even after 20 000 cycles at a high current density.

Flexible and semitransparent devices are highly attractive for powering display devices. To accomplish this goal, Liu \textit{et al} have demonstrated a flexible and transparent supercapacitor with good electrochemical performance using ultrafine Co\textsubscript{3}O\textsubscript{4} nanocrystals manufactured via laser ablation in liquid [118]. The pseudocapacitor thus prepared exhibited high gravimetric and areal capacitances of 177 F g\textsuperscript{-1} and 6.03 mF cm\textsuperscript{-2}, respectively at a scan rate of 1 mV s\textsuperscript{-1}. It also demonstrated a long cycle life with 100\% retention even after 20 000 cycles. The bendability and transparent nature of the supercapacitor is depicted in figures 7(a) and (b), respectively. The transparent supercapacitor was able to light-up a LED (figure 7(c)) and displayed an optical transmittance of up to 51\% as shown in figure 7(d). The bending test carried out from 0\° to 150\° 100 times showed that there is no reduction in capacitance, hence can be a potential, flexible supercapacitor. Recently, Feng \textit{et al} have demonstrated a substrate-free hydrothermal method for the large-scale synthesis of sub-3 nm atomic layers of Co\textsubscript{3}O\textsubscript{4} nanofilms [119]. This synthesis method emphasized the renovation of cobalt–ammonia complexes and the combined effect of free NH\textsubscript{3} and nitrate to control film growth. Electrochemical tests performed on
Co$_3$O$_4$ nanofilms exhibited an ultrahigh specific capacitance of 1400 F g$^{-1}$. The specific capacitance of Co$_3$O$_4$ nanofilms showed only slight decay in capacitance after 1500 cycles. Nickel oxide (NiO), another pseudocapacitive material has shown great promise in energy storage due to its abundance, economic and benign nature, excellent chemical stability and high theoretical capacitance. A hard-template based synthetic procedure is also feasible for developing mesoporous NiO nanoribbons [120]. The hard-template method would help in achieving controlled morphology, suitable pore-size and large surface area for charge storage as shown in figure 7(e). Very high capacitance of 1260 F g$^{-1}$ at 1 A g$^{-1}$ can be achieved for the nanoribbons. Since the usage of templates for synthesizing nanostructures would be expensive on a larger scale, hence a facile solvothermal method can be adopted in combination with the calcination process to develop hierarchical mesoporous rose-like NiO nanostructures (figure 7(f)) [121]. Here, nickel acetate can be used as the nickel precursor and guanidine hydrochloride can be used as the precipitant of the weak base. The reported hierarchical mesoporous rose-like NiO nanosheets exhibited an excellent electrochemical performance with a high specific capacitance of 1860 F g$^{-1}$ at 1 A g$^{-1}$ with 92% capacitance retention at a current density of 10 A g$^{-1}$ after 5000 cycles.

**Transition metal-hydroxides**

Nickel hydroxide [Ni(OH)$_2$] is a promising electrode candidate for high-performance supercapacitors but the syntheses and electrochemical performance of Ni(OH)$_2$ electrodes are sub-standard. A low-cost, one step chemical co-precipitation method can be used for synthesizing coaxial CNT/Ni(OH)$_2$ nanocomposites [122]. The coaxial structure of the electrode provides a 3D structure for the full electrolyte access. The schematic representation for the synthesis of CNT/Ni(OH)$_2$ composite is shown in figure 8(a). The synthesis process initially involved surface oxidation of CNTs to produce the electrostatic stability for the colloidal dispersion. Initially, the precursor of Ni(OH)$_2$ was adsorbed over the CNTs because of the interfacial electrostatic interaction between nickel and oxygen functional groups present in the CNTs which was followed by temperature and time optimization to obtain a uniform coating of Ni(OH)$_2$ over CNT to obtain the nanocomposite architecture as shown in figure 8(b). The nanocomposite stored charges via redox and electric double layer mechanisms and displayed a high capacitance of 1368 F g$^{-1}$ at a scan rate of 20 mV s$^{-1}$. Mao et al have developed an adsorption hydrothermal strategy for *in situ* integration of Ni(OH)$_2$ into 3D nitrogen-doped graphene aerogel (NG) [123]. This method produced monolithic free-standing supercapacitor electrodes avoiding the possible dead-weight of polymeric binders or other conducting agents. When Ni(OH)$_2$ is directly incorporated into a 3D matrix of graphene, it offered large surface area and microporous architecture for facilitating faster ion-diffusion as well as charge transport. A high specific capacitance of 1748 F g$^{-1}$ was achieved for the Ni(OH)$_2$ electrodes. In this nanocomposite, graphene helped in maintaining the structural stability of the electrode. The NG/Ni(OH)$_2$ nanocomposite exhibited a stable cycle life of 10,000 cycles with 90% of capacitance...
retention. Recently, an easy and cost-effective green method for in situ fabrication of binder-free Ni(OH)2 hexagonal platelets on Ni foam (HNF) as supercapacitor electrodes with high performance [124]. The one-step hydrothermal synthesis process involved using only 15 wt% H2O2 aqueous solution and not involving any nickel salts, acids, bases, or post-treatments (figure 8(c)). The as-prepared HNF electrode with hexagonal platelets as shown in figure 8(d), when directly used as a supercapacitor electrode material demonstrated a high specific capacitance of 2534 F g\(^{-1}\) at a scan rate of 1 mV s\(^{-1}\) and excellent cycling stability with 97% capacitance retention after 2000 cycles.

Layered double-hydroxide synthesized using two different hydroxides can provide synergistic charge storage capabilities [125–127]. Guo et al. have developed a hierarchical well-aligned NiMn-layered double-hydroxide (NM-LDH) nanosheets on nickel foam (NF) by a one-step wet-method in which urea hydrolysis supplies alkali and carbonate ions [125]. The as synthesized NiMn-LDH possessed highly oriented layered structure with ultrathin nanosheets. The molar ratio of Ni to Mn was optimized to obtain a maximum specific capacitance of 1511 F g\(^{-1}\) at 2.5 A g\(^{-1}\), a good rate capability by maintaining 80.1% retention when cycled at a very high current density of 48 A g\(^{-1}\) and a long cycle life of 3000 cycles by retaining 92.8% of its initial capacitance. A facile strategy using dodecylsulfate anions and graphene sheets as structural and conducting supports for developing integrated porous Co–Al hydroxide nanosheets (CA-LDH) has been recently reported [128]. The CA-LDH nanosheets provide a mesoporous integrated structure which found vital in fast ion/ electron transport. The electrode architecture helped CA-LDH electrodes in delivering a high specific capacitance of 1043 F g\(^{-1}\) at 1 A g\(^{-1}\) and ultra-high rate capability by delivering a capacitance of 912 F g\(^{-1}\) at 20 A g\(^{-1}\). The asymmetric supercapacitor fabricated with sandwiched graphene nanosheets (GNS)/porous carbon/CA-LDH delivered a high energy density up to 20.4 W h kg\(^{-1}\) at a very high-power density of 9.3 kW kg\(^{-1}\).

Chen et al. have developed ultrathin and porous nanosheets of nickel–cobalt layered double-hydroxide (NC-LDH) films via a facile and novel one-step synthesis using a growth agent, cetyltrimethylammonium bromide [129]. This electrode delivered a very high capacitance of 2682 F g\(^{-1}\) at 3 A g\(^{-1}\) and energy density of 77.3 W h kg\(^{-1}\) at a power density of 623 W kg\(^{-1}\). The reason for obtaining such an outstanding electrochemical performance are attributed to the quasi vertically aligned NC-LDH nanosheets on the nickel surfaces thus providing accessibility of electrolyte to all the nanosheets. The direct growth of the material avoided the use of electronically insulating binders. A strong layered orientation in the crystalline bimetallic hydroxides allows for effective electron transport from electrode-active material to current collector and thus allowing Ni(OH)2 and Co(OH)2 contribute efficiently to the pseudocapacitance. An asymmetric supercapacitor fabricated with NC-LDH as cathode and graphene-oxide as anode delivered a very high energy density of 188 W h kg\(^{-1}\) (well matched with lithium-ion batteries) with a power density of 1499 W kg\(^{-1}\).

**Transition metal-nitrides**

An asymmetric supercapacitor fabricated with metal-nitrides as the anode (Fe2N) and cathode (TiN) where the electrodes are synthesized via atomic layer deposition showed a specific capacitance of 58 F g\(^{-1}\) [130]. During the preparation of electrodes, before depositing the active materials, the CF substrate was coated with vertically aligned GNS to increase the surface area of the electrode. The active material precursors were deposited on to this substrate and thermally annealed in NH3 atmosphere to obtain porous nanostructures. Both transition metal-nitrides are highly electrically conducting which substantially improved the electronic and ionic-transport rate with a stable rate capability. The asymmetric supercapacitor fabricated with a gel electrolyte, polyvinyl alcohol (PVA)/lithium chloride exhibited 99% capacitance retention and 100% columbic efficiency at the end of 20,000 cycles. As shown in figure 9, the SEM images before and at the end of 20,000 cycles showed its high structural stability maintaining the porous structure and stable morphology. A high volumetric energy density of 0.61 mW h cm\(^{-3}\) was achieved at a power density of 52.9 mW cm\(^{-3}\). A table comprising the characteristics of mesoporous carbons-based supercapacitor electrodes in terms of synthesis method, surface area, pore-size, active-mass loading, specific capacitance, rate capability, and cycling stability is given in table 2.

Balamurugan et al. have fabricated an asymmetric supercapacitor using NG encapsulated nickel cobalt nitride (NiCo2N) (NCN) and NG encapsulated nickel iron nitride (NiFeN) (NFN) electrodes displayed an outstanding cycle life of 25,000 cycles with only 5.07% drop in its initial capacitance [131]. An improved cycle life was obtained through a unique core/shell structure developed via pyrolyzing a mixture of graphene-oxide, metal sources and cyanamide under an argon atmosphere at a temperature of 800 °C. The SEM images depicted in figures 10(a) and (b) show that NCN@NG and NFN@NG exhibit unique 3D hierarchical mesoporous architecture with nanoparticles-interconnected with each other providing open porous networks. The NG shell around the ternary metal-nitride prevents aggregation of nanoparticles and enhances the catalytic activity as well as electronic conductivity. An asymmetric supercapacitor fabricated with NCN@NG and NFN@NG electrodes delivered an ultrahigh energy density of 94.93 W h kg\(^{-1}\) at a power density of 0.79 kW kg\(^{-1}\) (figure 10(c)). The cycling stability was evaluated on five asymmetric supercapacitors showed an average capacitance degradation of 2.6% even after 25,000 cycles (figure 10(d)).

**Hybrid supercapacitors (battery-type)**

The ongoing research on both symmetric and asymmetric supercapacitors shows that new strategies must be implemented to obtain high energy density comparable to lithium-ion batteries. Hence, a new strategic design of HSCs using battery-type electrodes have been originated [132–137]. This
is a new supercapacitor electrode design such that one of the electrodes is a supercapacitor electrode and the other electrode is a battery-type. This type of electrode configuration in supercapacitors helps in obtaining high energy as well as power densities by combining the merits of both supercapacitor and battery electrodes. HSC utilizing battery electrodes can bridge the gap between conventional supercapacitors and lithium-ion batteries. They exhibit a high specific capacitance, excellent rate capability and long cycle life and have great potential in applications such as in hybrid electric vehicles, smart grids, etc [138, 139]. A detailed review in this topic is beyond the scope of this review hence in this section we briefly only discuss the development of various HSCs utilizing transition metal-oxides and hydroxides as positive and negative electrode-active materials.

Lithium-ion storage performance of transition metal-oxides is limited by the poor lithium-ion conductivity, inferior electronic conductivity, and the volume effect. These demerits can be rectified using nanocrystallization of transition metal-oxide particles [140]. Zhang et al have followed a room temperature precipitation in aqueous solution, followed by calcination method to develop V$_2$O$_5$ hierarchical spheres composed of stacked platelets as shown in figure 11(a) [141]. These spheres had mesopores of approximately 18.2 nm in diameter, and they showed good capacity up to 473 C g$^{-1}$ at 0.2 A g$^{-1}$ in 1 M LiNO$_3$ owing to their fast ion transfer speed between electrode and electrolyte. Figure 11(b) represents the typical CV curves of the V$_2$O$_5$//AC HSC device at different scan rates in a 1.6 V potential window. The CV curves with redox peaks show that the charge storage is basically via redox reactions. The HSC delivered a maximum specific capacitance of 0.26 F cm$^{-2}$ at 10 mVs$^{-1}$ and an energy density of 0.32 W h m$^{-2}$ at power density of 4.5 W m$^{-2}$.

Computer modeling has revealed that partial replacement of oxygen in metal-oxides with anions such as N$_3^-$, S$_2^-$, Cl$^-$, and F$^-$ can improve the rate capability and cycle life. Karthikeyan et al have developed Iron oxide (Fe$_2$O$_3$) nanomaterial with Floruide (F$^-$) substitution as electrode (F–Fe$_2$O$_3$) for HSCs [142]. A HSC fabricated with this F–Fe$_2$O$_3$ and AC delivered a specific capacitance of 71 F g$^{-1}$ at a current density of 2.25 A g$^{-1}$. This HSC had a good cycling stability after 15 000 cycles retaining 90% capacitance. Furthermore, the F–Fe$_2$O$_3$//AC device delivered a high energy density of about 28 W h kg$^{-1}$ at a power density of 0.55 kW kg$^{-1}$. Wang et al have reported a facile hydrothermal synthesis process for orthorhombic-phase niobium oxide (T-Nb$_2$O$_5$) nanowire structure with ultrathin carbon-coating as the anode for a HSC [143]. The nanowire structure showed a stable high rate Li$^+$ ion storage ability with 186.8 mA h g$^{-1}$ at 0.5 C and retaining 140.1 mA h g$^{-1}$ at 25 C. A HSC built with the AC showed a 3 V window with an energy density of 43.4 W h kg$^{-1}$ and a high-power density of 7.5 kW kg$^{-1}$. Another approach involves the synthesis of urchin-like rutile TiO$_2$ as the anode for HSCs via hydrothermal process [140]. Various nanostructures of TiO$_2$ powders such as anatase, nanorods, flower-like, and urchin-like TiO$_2$ powders were developed and compared. SEM image of urchin-like TiO$_2$ powder shown in figure 11(c) has a high specific surface area of
<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesis</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Specific capacitance</th>
<th>Rate capability</th>
<th>Cycle stability (retention %)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMoO₄ and CoMoO₄</td>
<td>Hydrothermal</td>
<td></td>
<td>1483 F g⁻¹ and 452 F g⁻¹ at 2 A g⁻¹</td>
<td>63.5% and 78.8% at 12 A g⁻¹</td>
<td>93.1% and 95.9% after 2000 cycles</td>
<td>[107]</td>
</tr>
<tr>
<td>MnO₂, SnO₂ and NiO nanorods</td>
<td>Solution process + calcination</td>
<td>156, 127 and 209</td>
<td>964 F g⁻¹, 745 F g⁻¹ and 620 F g⁻¹ at 2 A g⁻¹</td>
<td>81%, 84% and 81% at 20 A g⁻¹</td>
<td>91.8%, 90.5% and 90.3% after 10 000 cycles</td>
<td>[108]</td>
</tr>
<tr>
<td>MnO₂@MWCNT fiber</td>
<td>CVD + solution process</td>
<td></td>
<td>63.9 F cm⁻³ at 0.2 A cm⁻³</td>
<td>69% at 20 A cm⁻³</td>
<td>90% after 15 000 cycles</td>
<td>[115]</td>
</tr>
<tr>
<td>Manganese oxide nanococoons</td>
<td>Green over-reduction annealing</td>
<td>379.7</td>
<td>305 F g⁻¹ at 2 mV s⁻¹</td>
<td>29% at 100 mV s⁻¹</td>
<td>91.8%, 90.5% and 90.3% after 10 000 cycles</td>
<td>[116]</td>
</tr>
<tr>
<td>Co₃O₄/RGO nanocomposites</td>
<td>Co-precipitation</td>
<td>119</td>
<td>784 F g⁻¹ at 1 A g⁻¹</td>
<td>55% at 5 A g⁻¹</td>
<td>90% after 5000 cycles</td>
<td>[117]</td>
</tr>
<tr>
<td>Co₃O₄ nanocrystals</td>
<td>Laser ablation in liquid</td>
<td></td>
<td>1049 F g⁻¹ at 1 mV s⁻¹</td>
<td>57% at 20 mV s⁻¹</td>
<td>97.1% after 1500 cycles</td>
<td>[118]</td>
</tr>
<tr>
<td>Co₃O₄ nanofilms</td>
<td>Hydrothermal</td>
<td></td>
<td>1400 F g⁻¹ at 1 A g⁻¹</td>
<td>91.1% at 8 A g⁻¹</td>
<td>97.1% after 1500 cycles</td>
<td>[119]</td>
</tr>
<tr>
<td>Ribbon-like NiO</td>
<td>Hard-template</td>
<td>147</td>
<td>1260 F g⁻¹ at 1 A g⁻¹</td>
<td>59.4% at 20 A g⁻¹</td>
<td>95% after 5000 cycles</td>
<td>[120]</td>
</tr>
<tr>
<td>Roselike NiO nanosheets</td>
<td>Solvothermal</td>
<td>135</td>
<td>1860 F g⁻¹ at 1 A g⁻¹</td>
<td>48.2% at 20 A g⁻¹</td>
<td>92% after 5000 cycles</td>
<td>[121]</td>
</tr>
<tr>
<td>β-FeOOH nanorods</td>
<td>Hydrothermal</td>
<td>51.896</td>
<td>1094.74 F g⁻¹ at 1 mA cm⁻²</td>
<td>83% at 100 mA cm⁻²</td>
<td>100% after 5000 cycles</td>
<td>[104]</td>
</tr>
<tr>
<td>Ni-Co-Fe hydroxide</td>
<td>Electrochemical</td>
<td></td>
<td>1825 F g⁻¹ at 1 mV s⁻¹</td>
<td>68% at 25 mV s⁻¹</td>
<td>94% after 20 000 cycles</td>
<td>[110]</td>
</tr>
<tr>
<td>Ni(OH)₂ nanospheres</td>
<td>Electrochemical</td>
<td></td>
<td>2188 F g⁻¹ at 1 mV s⁻¹</td>
<td>43% at 20 mV s⁻¹</td>
<td>81% after 10 000 cycles</td>
<td>[111]</td>
</tr>
<tr>
<td>FeOOH quantum dots/graphene composite</td>
<td>Solution process</td>
<td></td>
<td>365 F g⁻¹ at 1 A g⁻¹</td>
<td>51% at 128 A g⁻¹</td>
<td>89.7% after 20 000 cycles</td>
<td>[112]</td>
</tr>
<tr>
<td>FeOOH nanoparticle</td>
<td>Hydrothermal</td>
<td>41</td>
<td>1066 F g⁻¹ at 1 A g⁻¹</td>
<td>74.6% at 30 A g⁻¹</td>
<td>91% after 10 000 cycles</td>
<td>[113]</td>
</tr>
<tr>
<td>CNT/Ni(OH)₂</td>
<td>Chemical precipitation</td>
<td></td>
<td>1368 F g⁻¹ at 20 mV s⁻¹</td>
<td>81% at 20 A g⁻¹</td>
<td>90% after 10 000 cycles</td>
<td>[122]</td>
</tr>
<tr>
<td>Nitrogen containing graphene/Ni(OH)₂</td>
<td>Adsorption-hydrothermal</td>
<td>95</td>
<td>741 F g⁻¹ at 0.2 A g⁻¹</td>
<td>81% at 20 A g⁻¹</td>
<td>90% after 10 000 cycles</td>
<td>[123]</td>
</tr>
<tr>
<td>Ni(OH)₂ hexagonal platelets</td>
<td>Hydrothermal</td>
<td></td>
<td>2534 F g⁻¹ at 1 mV s⁻¹</td>
<td>27.3% at 25 mV s⁻¹</td>
<td>97% after 2000 cycles</td>
<td>[124]</td>
</tr>
<tr>
<td>NiMn-LDH</td>
<td>Urea hydrolysis</td>
<td></td>
<td>1511 F g⁻¹ at 2.5 A g⁻¹</td>
<td>80.1% at 48 A g⁻¹</td>
<td>92.8% after 3000 cycles</td>
<td>[125]</td>
</tr>
<tr>
<td>Ni–Al LDHs/CNTs</td>
<td>Solution method</td>
<td>110</td>
<td>1500 F g⁻¹ at 1 A g⁻¹</td>
<td>70.3% at 10 A g⁻¹</td>
<td>50% after 2000 cycles</td>
<td>[127]</td>
</tr>
<tr>
<td>CoMn LDH film</td>
<td>Electrochemical</td>
<td></td>
<td>1062.6 F g⁻¹ at 0.7 A g⁻¹</td>
<td>69.2% at 28.6 A g⁻¹</td>
<td>96.3% after 5000 cycles</td>
<td>[126]</td>
</tr>
<tr>
<td>Co–Al hydroxide nanosheets</td>
<td>Anion intercalation, alkali etching, and electrostatic assembly</td>
<td>35.68</td>
<td>1043 F g⁻¹ at 1 A g⁻¹</td>
<td>87.4% at 20 A g⁻¹</td>
<td>88% after 3000 cycles</td>
<td>[128]</td>
</tr>
<tr>
<td>Material</td>
<td>Synthesis</td>
<td>Surface Area (m² g⁻¹)</td>
<td>Specific capacitance</td>
<td>Rate capability</td>
<td>Cycle stability (retention %)</td>
<td>References</td>
</tr>
<tr>
<td>----------</td>
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<td>------------</td>
</tr>
<tr>
<td>Ni-Co LDH</td>
<td>Hydrothermal co-deposition</td>
<td>2682 F g⁻¹ at 3 A g⁻¹</td>
<td>63.6% at 20 A g⁻¹</td>
<td>91.3% after 15 000 cycles</td>
<td>[129]</td>
<td></td>
</tr>
<tr>
<td>TiN@C</td>
<td>Hydrothermal + annealing</td>
<td>159 F g⁻¹ at 0.25 A g⁻¹</td>
<td>78.3% at 5 A g⁻¹</td>
<td>88% and 89% after 20 000 cycles</td>
<td>[114]</td>
<td></td>
</tr>
<tr>
<td>TiN porous layers and Fe₂N nanoparticles</td>
<td>ALD + annealing</td>
<td>180 F g⁻¹ and 170 F g⁻¹ at 10 mV s⁻¹</td>
<td>80% and 77% at 100 mV s⁻¹</td>
<td>98.16% and 97.69% after 20 000 cycles</td>
<td>[130]</td>
<td></td>
</tr>
<tr>
<td>NiCo₂N@NG and NiFeN@NG</td>
<td>Mixing + Pyrolysing</td>
<td>680 and 779</td>
<td>265 mAh g⁻¹ and 262 mAh g⁻¹ at 1 A g⁻¹</td>
<td>79.14% and 78.87% at 50 A g⁻¹</td>
<td>[131]</td>
<td></td>
</tr>
</tbody>
</table>
among other structures developed. Figure 11(d) shows the CV curves of all TiO$_2$ electrodes assembled with AC as an anode to construct a HSC. The HSC exhibited a high specific capacitance among all other structures with a value of 61.1 F g$^{-1}$. The HSC also exhibited a maximum energy density of 50.6 W h kg$^{-1}$ at a power density of 194.4 W kg$^{-1}$.

Meng et al have followed a sacrificial template method for developing hierarchical mesoporous NiO nanoarrays (NiO-NAs) with an ultrahigh capacitance of 3114 F g$^{-1}$ [144]. The synthesis process involved co-depositing Zn$^{2+}$ and Ni$^{2+}$ ions and etching the ZnO using an alkali to develop the mesoporous structure. The unique hierarchical mesoporous structure made sure that NiO is completely involved in the redox charge storage mechanism for obtaining the ultra-high capacitance. A HSC fabricated by using NiO-NAs as the positive electrode and macroporous graphene monoliths as the negative electrode has exhibited a maximum voltage of 1.6 V with a high energy density of 40.1 W h kg$^{-1}$ at a current density of 10 A g$^{-1}$. An aqueous HSC was fabricated with NCH a positive electrode and AC as a negative electrode to achieve an energy density of 40.1 W h kg$^{-1}$ at a power density of 801.2 W kg$^{-1}$. A 3D hierarchical porous flower-like nickel aluminum layered double hydroxide (NiAl-LDH) developed by a liquid-phase deposition on NF achieved a high specific capacity of 1250 C g$^{-1}$ at 2 A g$^{-1}$ with 76.7% retention after 5000 cycles at 50 A g$^{-1}$ [146]. The 3D flower-like structure provided pathways for ion and electron transport, which led to high capacity and excellent cycling stability even at high current density. A HSC fabricated with NiAl-LDH as the positive electrode and porous graphene nanosheet coated on NF as the negative electrode delivered a high energy density of 30.2 W h kg$^{-1}$ at a power density of 800 W kg$^{-1}$.

Generally, double metal-hydroxides possess high redox activity because of two metal components present in the compound. For example, Gou et al have developed a flower-like Ni–Co hydroxide (NCH) through chemical treatment of phosphite [145]. The double metal-hydroxide exhibited a specific capacitance of 1698 F g$^{-1}$ at 1 A g$^{-1}$ current density. It also delivered a good cycling stability 80.6% retention after cycling 4000 times at a current density of 10 A g$^{-1}$. A HSC fabricated with NiAl-LDH as the positive electrode and porous graphene nanosheet coated on NF as the negative electrode delivered a high energy density of 30.2 W h kg$^{-1}$ at a power density of 800 W kg$^{-1}$.
Another line of approach involves a two-step hydrothermal process for growing hierarchical flower-like NiAl-LDH directly on NF. This supercapacitor electrode can be further coated with 2D GNS nanosheet layers [147]. Coating GNS over LDH provides a conducting support, thus increasing faradaic charging and discharging of LDH, by efficiently improving the connection between LDH and the electrolyte. This would efficiently prevent the volume change in LDH during a long cycling process. A HSC developed using NiAl-LDH as positive electrode and GNS as negative electrode delivered an energy density 31.5 W h kg⁻¹ at a power density of 400 W kg⁻¹ and long-term cycle stability retaining 80% charging capability after 5000 cycles at 5 A g⁻¹. A monodispersed nickel-cobalt-oxide (NiCo₂O₄) prepared by flow atomization method with a mesoporous shell having a pore diameter of 2.5 nm is attractive for rapid transfer of electrolyte ions [148]. This led to a high electrochemical performance of the binary metal-oxide with a maximum specific capacity of 175 mA h g⁻¹ at 1 A g⁻¹ and a superior cycle life of 92.5% capacity retention after 50 000 cycles.

A HSC fabricated using NiCo₂O₄ as the positive electrode and nitrogen-doped mesoporous carbon as negative electrode material provided a working voltage of 1.5 V with a high energy density of 38.5 W h kg⁻¹ at a power density of 750.8 W kg⁻¹. The HSC was able to sustain a long-term cycle life of 20 000 with only 9.5% capacitance loss showing its potential as an efficient energy storage device. Another work on binary metal-oxides for HSC involves CuCo₂O₄ flowers synthesized on Ni-foam through a hydrothermal and post-calcination treatment [149]. These electrodes were able to deliver a high specific capacity of 179.2 mA h g⁻¹ at a scan rate of 1 A g⁻¹ with cycling life of 2000 with approximately 109% of the initial specific capacity retained. A table summarizing the HSC performance based on various electrode-active materials including mesoporous carbons, transition metal oxides, hydroxides and nitrides is given in table 3.

Device designs of supercapacitors

The grand vision for next-generation ubiquitous flexible electronic technology has already set an expected gross-market size of 16.5 Billion by 2021 [150], which in fact will cater our fantasy of embedded flexible electronic systems into reality in various form factors including wearables, e-paper, bendable/stretchable displays, environmental/biological sensors, and various health monitoring devices. However, the
Table 3. Summary of electrochemical performance of hybrid supercapacitor using mesoporous carbons, transition metal oxides, hydroxides and nitrides-based electrodes.

<table>
<thead>
<tr>
<th>Electrode combination in hybrid supercapacitor</th>
<th>Specific capacity</th>
<th>Specific energy density</th>
<th>Specific power density</th>
<th>Cycling stability (capacitance retention,%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen-doped activated carbons//Si/C</td>
<td>129 mA h g⁻¹ (185 F g⁻¹) at 0.4 A g⁻¹</td>
<td>230 W h kg⁻¹</td>
<td>30.12 kW kg⁻¹</td>
<td>76.3% after 8000 cycles</td>
<td>[133]</td>
</tr>
<tr>
<td>Nb₂O₅@C/rGO//AC</td>
<td></td>
<td>76 W h kg⁻¹</td>
<td>20.8 kW kg⁻¹</td>
<td>70% after 3000 cycles</td>
<td>[135]</td>
</tr>
<tr>
<td>Nb₂O₅/C//AC</td>
<td></td>
<td>74 W h kg⁻¹</td>
<td>18.51 kW kg⁻¹</td>
<td>90% after 1000 cycles</td>
<td>[136]</td>
</tr>
<tr>
<td>Graphene-wrapped Li₄Ti₅O₁₂//AC</td>
<td>83.6 F g⁻¹ at 0.1 mA cm⁻²</td>
<td>50 W h kg⁻¹</td>
<td>2.5 kW kg⁻¹</td>
<td>75% after 1000 cycles</td>
<td>[137]</td>
</tr>
<tr>
<td>3D-MnO/Carbon nanosheets//Carbon nanosheets</td>
<td></td>
<td>184 W h kg⁻¹</td>
<td>15 kW kg⁻¹</td>
<td>76% after 5000 cycles</td>
<td>[139]</td>
</tr>
<tr>
<td>TiO₂//AC</td>
<td></td>
<td>50.648 W h kg⁻¹</td>
<td>12.22 kW kg⁻¹</td>
<td>93% after 2000 cycles</td>
<td>[140]</td>
</tr>
<tr>
<td>V₂O₅//AC</td>
<td>0.26 F cm⁻² at 10 mV s⁻¹</td>
<td>0.32 W h m⁻²</td>
<td>45 W m⁻²</td>
<td>30% after 500 cycles</td>
<td>[141]</td>
</tr>
<tr>
<td>Fluorine doped Fe₂O₃//AC</td>
<td>71 F g⁻¹ at 2.25 A g⁻¹</td>
<td>28 W h kg⁻¹</td>
<td>3.5 kW kg⁻¹</td>
<td>90% after 15 000 cycles</td>
<td>[142]</td>
</tr>
<tr>
<td>T-Nb₂O₅//AC</td>
<td>34.8 F g⁻¹ at 0.25 A g⁻¹</td>
<td>43.4 W h kg⁻¹</td>
<td>7.5 kW kg⁻¹</td>
<td>82.3% after 3000 cycles</td>
<td>[143]</td>
</tr>
<tr>
<td>NiO//microporous graphene monoliths</td>
<td>188 F g⁻¹ at 0.4 A g⁻¹</td>
<td>67 W h kg⁻¹</td>
<td>6.41 kW kg⁻¹</td>
<td>89.6% after 6000 cycles</td>
<td>[144]</td>
</tr>
<tr>
<td>NiCo Hydroxide//AC</td>
<td>113 F g⁻¹ at 1 A g⁻¹</td>
<td>40.1 W h kg⁻¹</td>
<td>16.43 kW kg⁻¹</td>
<td>—</td>
<td>[145]</td>
</tr>
<tr>
<td>NiAl-LDH//graphene nanosheet</td>
<td>135.8 C g⁻¹ at 1 A g⁻¹</td>
<td>30.2 W h kg⁻¹</td>
<td>8 kW kg⁻¹</td>
<td>70% after 15 000 cycles</td>
<td>[146]</td>
</tr>
<tr>
<td>NiAl-LDH//GNS//GNS</td>
<td>141.9 C g⁻¹ at 0.5 A g⁻¹</td>
<td>31.5 W h kg⁻¹</td>
<td>8 kW kg⁻¹</td>
<td>80% after 5000 cycles</td>
<td>[147]</td>
</tr>
<tr>
<td>Nickel/cobalt oxide composite//nitrogen doped mesoporous carbon</td>
<td>123.2 F g⁻¹ at 1 A g⁻¹</td>
<td>38.5 W h kg⁻¹</td>
<td>21.4 kW kg⁻¹</td>
<td>91.5% after 20 000 cycles</td>
<td>[148]</td>
</tr>
</tbody>
</table>
vision is incomplete without developing efficient energy storage strategies, which should adhere with the future design requisites of high mechanical flexibility, high energy/power density, a wider temperature range of operation, long cycling life and cost-effectiveness. In this regard, the novel electrode materials and their hybrids described in the preceding sections are expected to be the best fit to the flexible energy storage model owing to their novel electrical, mechanical, and electrochemical performance. Depending on the type of application, new designs have been introduced for supercapacitor device development. Conventional supercapacitor designs are rigid, bulky and use liquid electrolytes. This limits its applications in miniaturized electronic devices.

In contrast, new solid-state supercapacitor designs use flexible electrodes and solid-state gel electrolytes. It can be easily shaped into thin, lightweight and smart designs, thereby increasing their potential for applications in flexible and wearable electronics. For brevity, we will focus only on the flexible supercapacitor designs and their applications in context to the next generation flexible electronics. In this section, we discuss three types of supercapacitor configurations such as sandwich-type, planar (micro) and yarn/fiber-type.

Sandwich-type supercapacitors

Sandwich-type configuration is one of the dominant supercapacitor designs, which comprises two similar or dissimilar flat electrodes separated by a gel electrolyte layer. Recently, a sandwich-type supercapacitor was assembled using highly flexible electrodes consisting of helically coiled CNTs grown on CFs [101]. The SEM, TEM and the selected area diffraction pattern of helically coiled defective-CNTs are shown in figures 12(a)–(c), respectively. A solid-state supercapacitor manufactured using PVA/lithium chloride gel electrolyte (figure 12(d)) used for preparing a flexible supercapacitor module (figures 12(e) and (f)) was able to light-up a white LED even at a bending angle of 180° (figures 12(g) and (h)). A flexible sandwich-type supercapacitor prepared recently based on laser-scribed graphene (LSG) electrodes on flexible PET substrates with polymer electrolyte [151]. This method presents a facile strategy to directly reduce GO films to graphene by using a low power infrared laser inside an inexpensive CD/DVD optical drive. This approach presents a binder-free integration of supercapacitor electrodes as well as avoids restacking of graphene sheets. This configuration offers an easy assembly and facile growth of active electrode materials directly on current collectors.

Semi-transparent sandwich-type energy storage devices are beneficial to be integrated with semi-transparent solar cells for light harvesting windows. To pursue this goal, an optically transparent and highly flexible symmetric solid-state supercapacitor was developed by assembling thin film electrodes of carbon nanocup in a highly porous 3D structure [36]. This device showed an optical transparency (71% at 550 nm wavelength), high volumetric power and energy densities of 19 mW cm⁻³ and 47 mWh cm⁻³ respectively. Since this method uses an anodic aluminum oxide template to achieve tailored geometry, a template-free electrode design is preferred. A direct filtration method was used to fabricate a Ni(OH)₂ intercalated graphene hybrid films as a positive...
electrode and CNTs incorporated into graphene nanosheets as the negative electrode [152]. The as assembled asymmetric supercapacitor exhibited a consistent capacitive performance upon subjecting to bending at different angles. This solid-state supercapacitor showed a high volumetric capacitance (58.5 F cm$^{-3}$) and high energy density of 9 W h kg$^{-1}$.

**Micro-supercapacitors**

Sandwich supercapacitor designs are often vulnerable to short circuits when no separator is used, or supercapacitor is subjected to various bending levels. At the same time, the easy transfer of charge carrier under strain is not well studied. Planar supercapacitors or micro-supercapacitors are being considered as an alternative configuration to sandwich supercapacitors as they provide size reduction, ease of fabrication, higher flexibility, and higher capacitance retention to fold, bend, or roll [153–155]. In planar supercapacitors, all three components, electrode material, electrolyte, and the current collector are integrated onto the same plane, offering fast ion transport channels in two-dimensions, which is essential for thin, flexible and bendable supercapacitors. Figure 13(a) shows an all solid-state flexible planar-integrated supercapacitor based on hierarchical zinc cobaltite (ZnCo$_2$O$_4$) nanowire/CFs electrodes coated by a PVA/phosphoric acid...
(H₃PO₄) electrolyte on a polyethylene terephthalate (PET) substrate with silver electrodes on either sides [156].

Flexible yet transparent electrochemical devices are getting increased recognition as the power source for next-generation electronic systems. For example, a novel comb-tooth type planar structure based on ZnO nanowires as anode for teeth type planar structure based on ZnO nanowires as anode/diode nanoscale photovoltaics and carbon nanoparticles as the cathode was demonstrated for flexible/smart/semitransparent supercapacitors [157]. The planar device was 45% transparent under visible spectrum and exhibited a high capacitance value of 2.89 F g⁻¹ without any degradation up to 10,000 charge-discharge cycles. The capacitance remained unchanged even after 100 bending cycles at a high bending radius of 10 mm.

The emerging miniaturization of electronic devices demands compact on-chip energy storage devices. Planar micro-supercapacitors fabricated using photolithography, and laser patterning technique have been fabricated for lab-on-chip compatibility [158]. Figure 13(b) shows the scalable fabrication of graphene micro-supercapacitors by direct laser writing on graphite oxide films using a standard light-scribe DVD burner [159]. Hundreds of LSG microelectrodes for micro-supercapacitors of different sizes can be fabricated on a single disc in just 30 min. Figure 13(c) shows the Ragone plot comparing the energy/power densities of laser-scribed micro-supercapacitors with commercially available supercapacitor devices.

Even though laser lithographic methods show great potential for next-generation lab-on-chip devices in CMOS and MEMS applications, they are expensive, tedious, and incompatible with flexible substrates for making micro-supercapacitors. Recently, template and non-template-based printing technologies have been adopted in designing printed electrochemical devices. Screen printing is a well-known template-based technique that utilizes a predesigned screen mesh which allows inks at low pressure to make desired image (figure 13(d)) [160]. This technique is being rapidly used for casting supercapacitors on textiles and garments. For example, a high capacity textile-based supercapacitor was fabricated by using screen printed AC ink onto knitted CF textile [161]. The device exhibited a very high capacitance of 0.51 F cm⁻² at a scan rate of 10 mV s⁻¹ and showed excellent electrochemical properties when tested in bending and stretching modes, making them viable for commercialization. Recently, high-performance AC and MWCNTs based supercapacitors (areal capacitance 74.2 mF cm⁻² at 1 mV s⁻¹) were screen printed directly on T-shirts using polymer gel electrolytes (figure 13(e)) [162]. These supercapacitors printed garments retained their performance even after washing, ironing (at 140 °C), and folding.

Among non-template printing methods, inkjet-printing and 3D printing can be used to make micro-supercapacitors. Unlike screen-printing, these techniques dispense ink directly on the receiving substrates without requiring a template and offer a non-contact digital printing for future printed electronics. A flexible solid-state micro-supercapacitor was developed via ink-jet printing of AC/CNTs electrodes and ionic electrolyte directly on conventional A4 paper using a commercial desktop inkjet printer [163]. The device displayed excellent mechanical flexibility, high cycling performance (no loss up to 10,000 cycles), and an energy density of 10 Wh kg⁻¹. In another study, a hybrid ink composed of graphene and commercial PEDOT:PSS was directly printed on ultrathin PET substrates to realize in-plane micro-supercapacitors (figures 13(f)–(h)) [164]. The as-prepared devices show great potential for wearables as capacitance loss was only 1.5% on continuous bending for 1000 cycles. Recently, a scalable fabrication method with high-resolution devices (feature size up to 20 μm) was proposed to design all-solid-state graphene micro-supercapacitors with a planar, interdigitated structure on flexible plastic substrates using a self-aligned printing process [165]. These devices exhibited an areal specific capacitance as high as 268 μF cm⁻² and excellent charge–discharge stability against mechanical deformation.

Yarn/fiber-type supercapacitors

Yarn/fiber-type supercapacitors are promising flexible supercapacitors receiving considerable attention owing to their novel design architecture and high energy density performance [52, 166–172]. Due to their 1D architecture, small volume and lightweight, they can be easily twisted, weaved, or stretched. They can render high fidelity with unconventional flexible electronics, which is not possible with the sandwich or planar supercapacitor designs. However, there are various fabrication strategies, different structures and novel device designs for fiber-type supercapacitors. A simple design of a fiber supercapacitor is shown in figure 14(a) that consists of two fiber electrodes, a helical spacer wire, and an electrolyte packaged in a plastic tube [173]. The spacer wire is used to provide separation between two electrodes as well as a scalable preparation. The fiber supercapacitor was highly bendable and can be wrapped over a glass rod (figure 14(b)). A variant of this configuration is developed by placing two fibers kept parallel to each other with some gap in between on planar substrates as support and filled with an electrolyte [174]. Figure 14(c) shows an all-solid-state flexible supercapacitor based on a carbon/MnO₂ core/shell fiber placed parallel to each other on a PET substrate covered by H₃PO₄/PVA solid-state electrolyte [175]. The flexible supercapacitor (figure 14(d)) exhibited a high rate capability at a scan rate up to 20 V s⁻¹, high volume capacitance of 2.5 F cm⁻³, and an energy density of 2.2 × 10⁻³ Wh cm⁻³.

Another cable supercapacitor design is one in the form of single-wire where one wire is wound around the other, and a gel electrolyte is filled in between them. Since most of the textile fibers (cotton, cellulose) used for wire- or yarn-based supercapacitors are non-conductive; dipping or coating of these fibers into metals or carbonaceous materials have been performed to induce high electrical conductivity and mechanical stability. A coaxial supercapacitor was designed using CuO@AuPd@MnO₂ core–shell nanowhiskers grown on Cu wire and foil as inner and outer electrodes, respectively [52]. This design offers large utilization of active materials providing significant energy storage as well as renders a high mechanical strength. It retained 93.4% of the initial charge
after bending 100 times at different angles from 0° to 180°. Nevertheless, 99% of its initial capacitance was maintained even after 5000 cycles at 100 mV s⁻¹. An essential attribute of this cable device is that in addition to the charge storage, it can be used to transmit electricity via the same cable. Yu et al. developed a coil-type asymmetric supercapacitor electrical cable using Fe₂O₃@C nanorods as the anode and CuO nanowhiskers@AuPd@MnO₂ as cathode following a similar strategy [176]. This coil-type ASC delivered a volumetric capacitance of 2.46 F cm⁻³ at a current density of 0.13 A cm⁻². A good bendable behavior was exhibited by the supercapacitor with 93% capacitance retention after 4000 cycles at different bending angles.

**Conclusion and perspective**

We have extensively reviewed various electrode materials for application in supercapacitors. In addition, various strategies adopted for improving supercapacitor performances like nanostructuring of the electrodes, HSC designs and flexible supercapacitors are discussed. The reviewed electrode materials include mesoporous nanomaterials such as nanostructured carbons, transition-metal oxides, transition metal-hydroxides, transition metal-nitrides, electronically conducting polymers; and their composites. Traditional carbon nanomaterials with mesoporous architecture include mesoporous carbons, mesoporous CNFs, CNTs, and their composites. The advantages of using carbon nanomaterials as electrodes in supercapacitors include good electronic conductivity, large surface area, excellent chemical and electrochemical stability, good mechanical strength, high cycle life, and excellent coulombic efficiency. Nanostructured transition metal-oxides such as MnO₂, Co₃O₄, NiO have made significant development in manufacturing supercapacitors with much better energy density and operating voltage than carbon-based materials. The improvement in capacitance is attributed to the possession of large surface area and excellent reversible redox-reactions. However, their poor electrical conductivity, inferior power density, and low cycle life are some of the challenges for its commercialization. The reason why transition metal-oxides/hydroxides-based electrodes underperform with respect to cycle life is due to its volume expansion/contraction during the charge-discharge process. The charge balance in the positive and negative electrodes has to be maintained to obtain the cyclability. Transition metal-nitrides are far better candidates for supercapacitors compared with transition metal-oxides/hydroxides; as they exhibit good electrical conductivity, excellent cycling stability, etc, but low capacitance is a significant drawback. These demerits associated with transition metal-oxides/hydroxides and nitrides can be surpassed by preparing composites either with carbon nanomaterials or with electronically conducting polymers. The feasibility of developing supercapacitors with various electrode materials are almost restricted due to its natural abundance and cost features; hence novel methods to improve the specific capacitance and energy density by developing novel electrolytes and environment-friendly materials are highly appreciated.

Recent advancements in the supercapacitor research clearly show that they have great potential in the field of energy storage as they can be integrated with a variety of microelectronic and other wearable devices. The operating voltage window of the supercapacitors is still a significant challenge with respect to safe and environment-friendly electrolytes. Aqueous electrolytes can be operated till a voltage window of 1.2 V if used in a symmetric configuration whereas organic electrolytes can operate above 2 V, but they are flammable and not environment-friendly. Asymmetric supercapacitor designs are much attractive due to the possibility of tuning the operating voltage window of the

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**Figure 14.** (a) Schematic of a fiber supercapacitor and (b) its high bendability represented by wrapping around a glass rod with a diameter of 7.5 mm. Reproduced with permission from [173] Copyright (2012) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) All solid-state flexible supercapacitor fabricated by placing electrodes parallel to each other on a flexible substrate, and (d) its ability to power a commercial LCD (left) and LED (right). Reprinted (adapted) with permission from [175] Copyright (2012) American Chemical Society.
supercapacitor as well as to achieve high energy density. Hybrid designs of supercapacitor electrodes help in attaining high specific capacitance and comparatively high energy density. Of course, there is no comparison with the existing lithium-ion batteries, still, the supercapacitors can achieve energy densities more than the minimum values reported for lithium-ion batteries. The recent development of HSCs utilizing both a supercapacitor electrode and a battery electrode is a better solution for the energy density issue pertaining to a conventional supercapacitor. Supercapacitors are not intended to replace the existing lithium-ion batteries but can be complementary to each other. Hybrid approach enables to close the gap between the supercapacitors and existing lithium-ion batteries in which supercapacitors can deliver high power whereas the latter can provide high energy density.

In future research, a complete understanding of the tenability in the electrode potentials by advanced techniques will be appreciated as it can widen-up the operating potential window in the case of asymmetric supercapacitor electrodes. Novel methods to improve the volume expansion/swelling of the supercapacitor electrodes in order to attain good cyclability and power density should be developed. In order to power the future electronic devices which are highly flexible and wearable, supercapacitors with high flexibility and good mechanical stability have to be developed. The capability of integrating the flexible supercapacitor with a wearable textile or other substrate depends on the weavability of the supercapacitor. Fibers/yarns-based supercapacitors are much attracted in this aspect that they can easily be integrated with wearable textiles during their manufacture. Also, the flexible supercapacitors open various other novel integrated energy conversion devices such as solar cell and nanotribogenerators in order to develop self-powered supercapacitor cables. This may find enormous applications in the future in various fields such as military, transportation, wearables, etc.

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