

Review

A Review of Electrospun Carbon Nanofiber-Based Negative Electrode Materials for Supercapacitors

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Abstract: The development of smart negative electrode materials with high capacitance for the uses in supercapacitors remains challenging. Although several types of electrode materials with high capacitance in energy storage have been reported, carbon-based materials are the most reliable electrodes due to their high conductivity, high power density, and excellent stability. The most common complaint about general carbon materials is that these electrode materials can hardly ever be used as free-standing electrodes. Free-standing carbon-based electrodes are in high demand and are a passionate topic of energy storage research. Electrospun nanofibers are a potential candidate to fill this gap. However, the as-spun carbon nanofibers (ECNFs) have low capacitance and low energy density on their own. To overcome the limitations of pure CNFs, increasing surface area, heteroatom doping and metal doping have been chosen. In this review, we introduce the negative electrode materials that have been developed so far. Moreover, this review focuses on the advances of electrospun nanofiber-based negative electrode materials and their limitations. We put forth a future perspective on how these limitations can be overcome to meet the demands of next-generation smart devices.

Keywords: electrospinning; negative electrode materials; carbon nanofibers; free-standing; supercapacitor



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1. Introduction

Electrical energy has been an indispensable aspect of human civilization. It is essential for day-to-day activities, developing infrastructures, discovering new technologies, and driving the economy. Currently, fossil fuels are the primary energy sources, contributing more than two-thirds of total electricity generation; however, global energy demand continues to increase [1–3]. Additionally, fossil fuels are the main contributor of CO₂ emissions that are responsible for life-threatening global warming. Moreover, fossil fuel sources are being rapidly exhausted and they are inherently non-renewable [4]. The above facts demonstrate the urgent need for renewable, clean, and sustainable energy sources, and research has moved in this direction. However, energy generated from renewable sources such as hydro, solar, and wind is intermittent, and there is a large fluctuation in energy output. Therefore, energy generated from these sources has to be stored so it can be supplied when and where it is needed. The development of efficient electrical energy storage technology that can store a large amount of energy from intermittent and fluctuating renewable sources has been one of the major obstacles to a fossil fuel-free, clean, and sustainable society [5]. Currently, batteries and supercapacitors (SCs) are two major

energy storage technologies. Li-ion batteries, with their high energy density ($\sim 300 \text{ W h kg}^{-1}$), have tremendously contributed to this field and were recognized with the Nobel prize in Chemistry 2019; however, batteries suffer from a limited operating life (a few thousand cycles), slow recharge rate, low power density, and safety issues [6,7]. SCs, due to their attractive features, such as their fast charge and discharge rates (s to min), high power density ($\sim 10^5 \text{ W kg}^{-1}$), and long operating life ($>10^6$ charge-discharge cycles), are a promising alternative or complement to batteries [8,9]. Moreover, SCs are better than batteries in regard to safety. Commercialized for the first time under the name “supercapacitor”, SCs are currently available for various applications. However, the widespread stand-alone utility of SCs has been limited mainly due to the low energy storage capacity per unit mass, volume, or area of their electrodes. Therefore, the current research approach is to increase the energy storing capacity of SCs without compromising their cycling life and power density mainly by developing efficient electrode materials [10]. Over the past decades, nanoscale carbon materials, conducting polymers, transition metal compounds, and their composites have been explored as electrode materials and have shown promising results. A large specific surface area, high electronic conductivity, and abundance of active sites are the primary requirements of active electrode materials. Additionally, high porosities and proper nanoarchitectures are other promising features [11–13]. Finally, being lightweight and flexible are additional requirements for portable, flexible, and wearable devices. Apart from these factors, the use of cost-effective and ecofriendly materials, availability of simple and fast fabrication processes, demonstration of multifunctional use, and capacity for mass production are parameters that are always at the center of commercial materials.

2. Negative Electrode Materials

Basically, a supercapacitor consists of two electrodes, namely, a positive electrode and a negative electrode that are separated by an electrolyte-rich semipermeable membrane identified as the separator. When comparing the energy density of an energy storage device, there is a very large gap between a battery and a supercapacitor device. A battery has a high energy density but a low power density, while a supercapacitor has exactly the opposite. Herein, obtaining a supercapacitor device with a high energy density is the main challenge, and this needs to be significantly improved to meet the increasing energy density demands of next-generation high-tech devices. It is well known that the energy density of a device depends on the working potential window of the device and the capacitance, as indicated by the formula, Energy density (E) = $1/2 CV^2$, where C is the capacitance and V is the working potential window. This demand further focuses on developing devices with a high capacitance that work over a wide potential range. Several thousands of studies have focused on the development of pseudocapacitor electrode materials with high capacitance. Pseudocapacitance is the combination of a capacitor-type material and a redox material. Generally, research on novel materials for supercapacitor applications is extremely active but is mostly done for positive electrode materials (cathodes). Wu et al. fabricated nickel-cobalt layered double hydroxide as a cathode material, which exhibited 2682 F g^{-1} at a current density of 3 A g^{-1} [14]. In another work, Liang et al. [15] fabricated an oxygen vacancy-rich nickel-cobalt layered double hydroxide electrode that demonstrated 1563 F g^{-1} capacitance at a current density of 1 A g^{-1} . However, the common properties of metal-based positive electrode materials are that they work within small potential ranges (0–0.5/6 V) [14–17]. This result means that the assembly of a supercapacitor device by using only the above materials cannot lead to a high enough energy density. On the other hand, carbon-based materials have been used as anodes that work over a wide range of negative potentials while demonstrating lower capacitance values than cathode materials. The assembly of a positive electrode material with carbon-based materials as the asymmetric supercapacitor device significantly improves the energy density of the device due to the synergistic effect of both types of electrode materials. Hence, the development of anode materials that have relatively high capacitance but work over a wide potential window is imperatively important. In this regard, several attempts have been made to

obtain anode materials with desirable properties. The major negative electrode materials include tin-based [18,19], copper-based [20], vanadium-based [21,22], MO-based [23,24], iron-based [25–27], and carbon-based electrode materials [28–32] (Table 1). We review the carbon fiber-based negative electrode details in this report.

Compared to carbon-based materials, metal-based negative electrode materials have been reported to show superior capacitance values. The major concerns of metal-based materials are the phase changes that occur due to the redox activity during long-term use and their low conductivity, notably limiting their uses [33–35]. Thus far, only carbon materials have been used in commercial electrical supercapacitor devices due to their excellent stability under various conditions, such as pH and temperature. Moreover, carbon materials have desirable properties, such as a large surface area and outstanding conductivity, compared to metal-based electrodes. The major carbon materials are activated carbon (AC) [36,37], carbon nanotubes (CNTs) [38,39], graphene [40], carbon cloth (CC) [41], electrospun carbon nanofibers [32,42,43], porous carbons [44–46], and their composites (Table 1).

Table 1. List of negative electrode materials reported in the literature.

S.N.	Electrode Materials	Electrolyte	Capacitance	Current density	Reference
1.	Iron phosphide (FeP) nanotubes	1 M LiCl	149.11 F g ⁻¹	1 mA cm ⁻²	[27]
2.	Activated CNF	6M KOH	156.0 F g ⁻¹	0.5 A g ⁻¹	[31]
3.	Carbon-coated tin nitride (TiN)	1 M KOH	167.0 F g ⁻¹	1 A g ⁻¹	[19]
4.	80:20 PAN, Poly(acrylonitrile-co-butadiene (PAN/PAN-co-PB) derived CNF	2 M KOH	172.0 F g ⁻¹	1 A g ⁻¹	[29]
5.	CNF/graphene	6 M KOH	183.0 F g ⁻¹	1 A g ⁻¹	[47]
6.	ZIF-8 derived nanoporous carbon (ZIF-8/NPC)	3 M (KOH)	190.0 F g ⁻¹	1 A g ⁻¹	[45,48]
7.	Nitrogen-doped hollow activated carbon nanofibers (HACNFs)	6 M KOH	197.0 F g ⁻¹	0.2 A g ⁻¹	[49]
8.	Nitrogen doped NCFs@polypyrrole (NCNF-900@PPy)	6 M KOH	202.0 F g ⁻¹	1 A g ⁻¹	[50]
9.	Three-dimensional porous CNFs (P@3D-CNF)	2 M KOH	205.5 F g ⁻¹	1 A g ⁻¹	[28]
10.	ZIF-7/glucose composite-derived carbon-L-950	6 M KOH	228.0 F g ⁻¹	0.1 A g ⁻¹	[46]
11.	Graphene/carbon nanotube/iron oxide (G/CNT/Fe ₂ O ₃ -150)	1 M Li ₂ SO ₄	258.0 F g ⁻¹	1 A g ⁻¹	[51]
12.	CNF-40 (Polystyrene foam/PAN, PF: PAN = 40:60)	1 M H ₂ SO ₄	271.6 F g ⁻¹	0.5 A g ⁻¹	[52]
13.	Vanadium pentoxide V ₂ O ₅ /vertically aligned CNTs composites (V ₂ O ₅ /VACNT)	1 M sodium sulphate (Na ₂ SO ₄)	284.0 F g ⁻¹	2 A g ⁻¹	[21]
14.	Three dimensional boron-doped CNF (3D-BN-CNF-F900)	2 M KOH	295.0 F g ⁻¹	0.5 A g ⁻¹	[42]
15.	Porous CNF-3	6 M KOH	314.0 F g ⁻¹	0.5 A g ⁻¹	[53]
16.	Reduced graphene oxide-CNF (rGO-CNF, 1:1)	6 M KOH	316.5 F g ⁻¹	0.25 A g ⁻¹	[43]

Table 1. Cont.

S.N.	Electrode Materials	Electrolyte	Capacitance	Current density	Reference
17.	PAN: poly(m-aminophenol (PmAP)-NCNF	6 M KOH	347.5 F g ⁻¹	0.5 mA cm ⁻²	[54]
18.	Porous CNFs	6 M KOH	362.0 F g ⁻¹	0.2 A g ⁻¹	[55]
19.	hierarchical porous carbon nanotube (HPCT)	6 M KOH	386.2 F g ⁻¹	0.1 A g ⁻¹	[56]
20.	CNT@Graphene	6 M KOH	401.0 F g ⁻¹	1 A g ⁻¹	[30]
21.	Molybdenum oxide/sulphide (MoO ₂ /MoS ₂)	1 M Na ₂ SO ₄	433.3 F g ⁻¹	5 mV s ⁻¹	[23]
22.	CNT@CNF	6 M KOH	464.2 F g ⁻¹	0.5 A g ⁻¹	[57]
23.	Electrodeposited molybdenum oxide (MoO _x) film	1 M H ₂ SO ₄	507.0 F g ⁻¹	1 A g ⁻¹	[24]
24.	Carbon nanotube@graphene-CNFs (CNT@Gr-CNF-5)	6 M KOH	521.5 F g ⁻¹	0.25 A g ⁻¹	[39]
25.	Amorphous cobalt phosphate/porous carbon on CC (a-PC@CoPi-CC8)	2M KOH	606.1 F g ⁻¹ (2.15 F cm ⁻²)	1 A g ⁻¹ (4 mA cm ⁻²)	[58]
26.	Tantalum in copper sulphide (Ta-Cu ₇ S ₄)	1 M KOH	675.0 F g ⁻¹	1 A g ⁻¹	[20]
27.	3D Titanium Carbide (Ti ₃ C ₂) aerogel	1 M KOH	1012.0 mF cm ⁻²	2 mV s ⁻¹	[18]
28.	Vanadium oxides (VO _x)	5 M lithium chloride (LiCl)	1.57 F cm ⁻² 1652.3 F g ⁻¹	2 mA cm ⁻²	[22]

3. Carbon-Based Negative Electrode Materials

The conventional electrode material for electrical double-layer capacitors (EDLCs) is porous AC with a large specific surface area of ~2500 m² g⁻¹, which delivers capacitances of 200 F g⁻¹ and 100 F g⁻¹ in aqueous and organic electrolytes, respectively [36,59]. Graphene is a promising material as a negative electrode [32,60]. A three-dimensional exfoliated graphene network has a mesoporous structure and excellent conductivity, enabling a high capacitance of up to 330 F g⁻¹ that is superior to other AC-based electrodes [61]. However, the highly expensive or tedious work needed to synthesize graphene can hinder their large-scale production and practical use. This is the same case for CNTs. The more common aspect of graphene, CNTs, or activated carbon is that these electrode materials can hardly be used as free-standing electrodes and their surfaces are difficult to modify due to their powdered form and tendency to quickly aggregate. Self-supported electrode materials are necessary to make a device function independently. CC is promising as a self-supporting highly conductive substrate with high strength and flexibility. However, CC by itself has an extremely low capacitance due to its small surface area (<10 m² g⁻¹) and larger size compared to nanostructured materials. Recently, the activation of CC to increase its surface area has been considered a prominent strategy for achieving anode materials with a high capacitance [62]. Increasing the surface area of a material is a prime strategy since the surface is involved in ion adsorption and desorption at the electrode-electrolyte interface of an EDLC [63,64]. Moreover, the functionalization of carbon cloth materials also improves their performance by increasing conductivity and accommodating other double layer capacitance-contributing materials [65–67]. Porous nitrogen-doped carbon cloth exhibits a capacitance of 190 F g⁻¹ [68]. Heterodoping on a mesoporous and functionalized CC can further increase the capacitance while exhibiting a wide working potential [58]. Tiwari et al. [58] reported an amorphous cobalt phosphate particle-anchored CC with N-P-doped porous carbon that delivered a capacitance of 606.1 F g⁻¹ at a current density of 1 A g⁻¹, which is significantly higher than that of the corresponding nonfunctionalized

materials. Furthermore, these electrodes work over a wide potential range (-1.4 to $+0.5$) in an aqueous KOH electrolyte (Figure 1), thereby opening a new avenue to produce a high-performance symmetrical supercapacitor. Moreover, they have shown that the as-assembled symmetrical device exhibited an energy density up to 31.1 W h kg^{-1} at a power density of 476.0 W kg^{-1} while demonstrating exceptional stability (94.2%). The superior performance of the above device among contemporary devices was attributed to the amorphous carbon/cobalt phosphate composite and additional doping of P. Another report also suggested that doping P in amorphous materials can widen the working potential window, thereby increasing the energy density of the device [69].

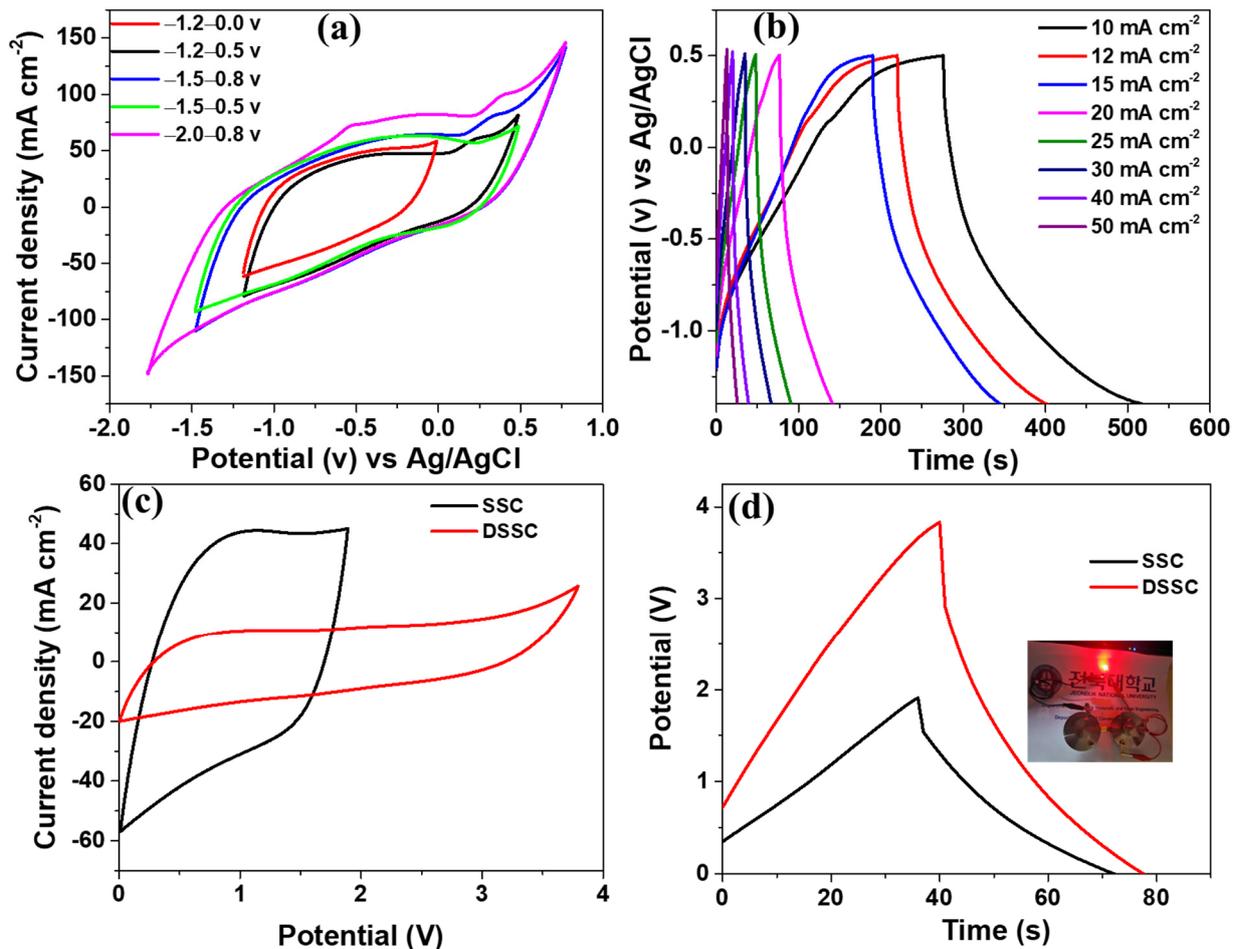


Figure 1. CV curves of a-PC@CoPi-CC8 within different potential windows at 50 mV s^{-1} (a), GCD curves of the same sample at different current densities at potential ranges from -1.4 to 0.5 (b). CV profiles of a symmetric supercapacitor (SSC) and a double SSC (DSSC) assembled from a-PC@CoPi-CC8 and collected at 50 mV s^{-1} (c), and GCD curves of the SSC and DSSC devices collected at 20 mA cm^{-2} (d). Inset is the image of a red light-emitting diode (LED) powered by two SSCs in series. The supercapacitor devices were charged for approximately 40 s before the LED tests. Reprinted with permission [58].

4. Electrospun-Based Fibers as Negative Electrode Materials for Supercapacitors

Currently, electrospun carbon nanofibers (ECNFs) have appeared as a promising material for electrochemical energy storage [32,38,59]. Most importantly, electrospun fibers can be produced with a simple machine in a laboratory setting, unlike the need for a company set up to produce carbon cloth. CNFs can be fabricated by the cost-effective and convenient electrospinning of organic polymers followed by carbonization [70–72]. Electrospinning is a method for the facile fabrication of nanofibers under the influence of an external electric field. It allows the fabrication of continuous fibers with nano- to

microscale diameters [73–75]. In 1887, C. V. Boys showed that fibers could be produced from a viscoelastic liquid in the presence of an external electric field [76]. In 1902, J. F. Cooley and J. Martin filed patents for a prototype setup for electrospinning [71]. In 1964–1969, Geoffrey Taylor reported a mathematical model for the formation of a Taylor cone from a spherical solution droplet under the influence of an external electrical field [77–79]. After the 1990s, various organic polymers were demonstrated to form nanofibers, and, after the 2000s, composites, ceramics, core-shell structures, hollow structures, and various types of nanofibers were produced [80–84]. Currently, electrospinning is a versatile method for the facile production of nanofibrous structures with diverse structures and functionalities for a variety of advanced technologies. The morphology, structure, and functionality of the nanofibrous material are determined by the nature of the polymer, solvent, and processing parameters [85,86]. Currently, a large number of natural and synthetic polymers have been successfully reported for the fabrication of nanofibers by electrospinning [71]. By incorporating active nanomaterials or precursors, electrospun nanofibers can be used as advanced functional materials for a variety of technologies, such as air filtration, including face masks, water filtration; oil-water separation; energy storage and conversion; catalysis; biomedical use; textiles. The postmodification of nanofibers is essential for obtaining structural and functional variations, as demanded by various technologies. A typical electrospinning setup is illustrated in Figure 2.

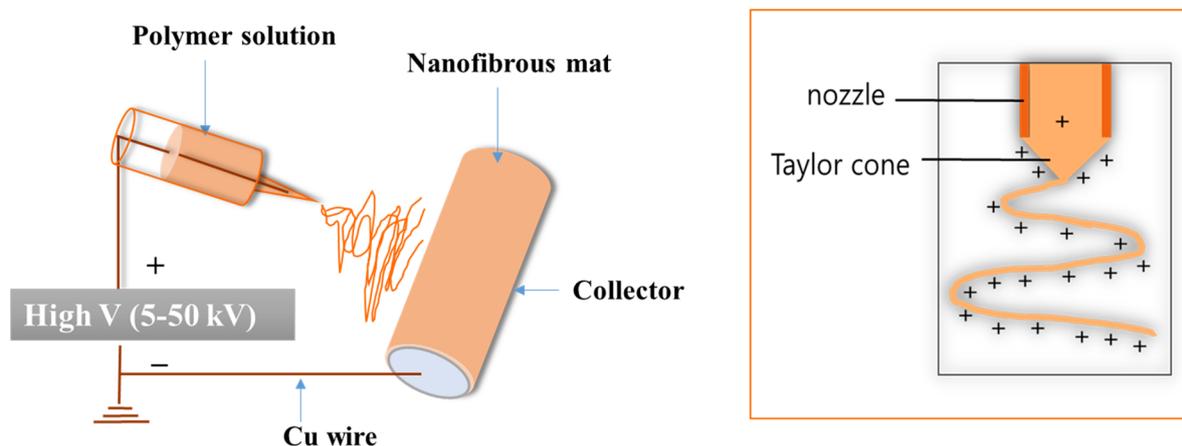


Figure 2. Schematic representing the simple electrospinning process.

CNF sheets consist of very long nonwoven one-dimensional (1D) carbon nanofibers that form 2D sheets that can be modified as necessary. The large specific surface area, chemical stability, lightweight, good conductivity, easy accessibility, and environmentally friendly nature of CNFs are attractive features. In addition, CNFs possess other advantages: (i) CNFs are very economical compared to graphene and carbon nanotubes and can be easily fabricated on a mass scale. (ii) With proper modifications of the electrospinning technique, precursor composition, or position, followed by a postmodification, carbon nanofibers with extraordinary porosity, a large specific surface area, and diverse functionalities can be fabricated [87–92]. (iii) CNFs can be directly used as a free-standing electrode without the use of a conductive additive, binder, or current collector. The use of binders and additives decreases the effective surface area and conductivity of the electrode, thereby decreasing its performance [93]. ECNF sheets as current collectors instead of heavy metals, such as nickel foam, significantly reduce the weight of electrodes [94,95]. (iv) CNF sheets offer a light and chemically stable 1D nanoskeleton for the growth of various active nanostructures in 3D patterns without aggregation and can be used as free-standing electrodes [96,97]. (v) CNFs offer a larger specific surface area and conductive network than the same mass of carbon cloth since the fibers in carbon cloth are microscale. (vi) Finally, CNFs can be used as flexible electrodes. Therefore, electrospun carbon nanofiber sheets are very attractive for energy

storage applications [98,99]. Moreover, the modification of CNFs to obtain an increased capacitance can be done in two ways. First, the electrospinning process is performed by tuning the electrospinning solution parameters and processing parameters. Second, modifications can be done by post-CNF synthesis processes [32,59]. The post-modification approaches for increasing capacitance are more or less similar to those of CC.

The most commonly used polymer to synthesize carbon nanofibers is PAN due to its high carbon yield compared to other polymers. Other polymers used for that purpose are shown in Table 2. Various processing parameters, such as the voltage, flow rate, and collector-to-tip distance, along with solution parameters, such as the viscosity and conductivity of a polymer solution, can play a role in controlling the morphology and fiber diameter of the final product. Pure, as-spun polymeric nanofibers generally have low conductivity; therefore, stepwise thermal treatment processes, such as stabilization and subsequent carbonization, must be performed to make the carbon fibers more conductive. The potential of electrospun carbon nanofiber-based materials in diverse advanced technologies has been increasingly studied, and progress has been summarized in a few reviews. However, works related to electrospun carbon nanofiber-based negative electrode materials for supercapacitors have been rarely summarized. We believe this review can serve as a resource for further studies on the development of negative electrode materials for high-performance energy storage devices.

Typically, ECNFs are solid and have a small surface area that results in low capacitance and energy density. To this end, it is necessary to design carbon fibers to increase the surface area and make composites with materials that can contribute to a high capacitance, while not hampering the inherent features of carbon fibers. Nanofibrous materials with a high specific surface area, controllable porosity, good conductivity, and flexibility are promising features for next-generation technologies. Therefore, different strategies have been adopted to fabricate nanofibers with such properties. Coaxial electrospinning produces sheath-core nanofibers. It uses a coaxial needle that consists of inner and outer hollow needles that are arranged concentrically and dispense two different solutions. By using less volatile or washable core polymers, hollow nanofibers can be obtained [83]. Coaxial electrospinning using poly(methyl methacrylate) (PMMA) as the core solution and a PAN solution as the shell solution, thereby producing PMMA/PAN core-shell nanofibers. Regarding the PMMA/PAN nanofibers after carbonization, a more volatile PMMA portion is removed; therefore, hollow carbon nanofibers are obtained (Figure 3b) [88]. Electrospinning PAN/PMMA blends with different ratios produce multiporous nanofibers (Figure 3c) [100].

Using block copolymer-based precursors as an approach is significant for controlling the porosity of the resulting material and may revolutionize the synthesis of PCNFs [91]. Zhou et al. synthesized dual-doped PCNFs with well-controlled bimodal pores, namely, mesopores (10 nm) and micropores (0.5 nm), by electrospinning poly(acrylonitrile-block-methyl methacrylate) (Figure 3f) [91]. There are some other notable reports. Yan et al. prepared highly porous sponge-like carbon nanofibers by electrospinning poly(tetrafluoroethylene) and poly(vinyl alcohol) with boric acid as the cross-linking agent. These nanofibers possessed well-controlled macro/meso/micropores and an ultrahigh porosity (>80%) and outstanding conductivity (980 S cm^{-1}), while being triple-doped with B-F-N (Figure 3g) [103]. Yang et al. prepared necklace-like hollow carbon nanofibrous materials with an abundance of micro/meso/micropores and an ultrahigh content of doped N (Figure 3h) [104]. One of the common strategies for fabricating porous nanofibers is the selective removal of a sacrificial phase from the as-spun nanofibers by washing, leaching, or heating. The sacrificial phase may be small nanoparticles or another polymer. Wang et al. fabricated silicon oxide (SiO_2)- and Sb-entrapped nanofibers by electrospinning antimony trichloride (SbCl_3), polyvinylpyrrolidone (PVP), and tetraethylorthosilicate (TEOS). After carbonization and etching with HF, a highly porous carbon nanofibrous structure was obtained (Figure 3d) [102]. They later used this electrode as a highly stable electrode for Li batteries.

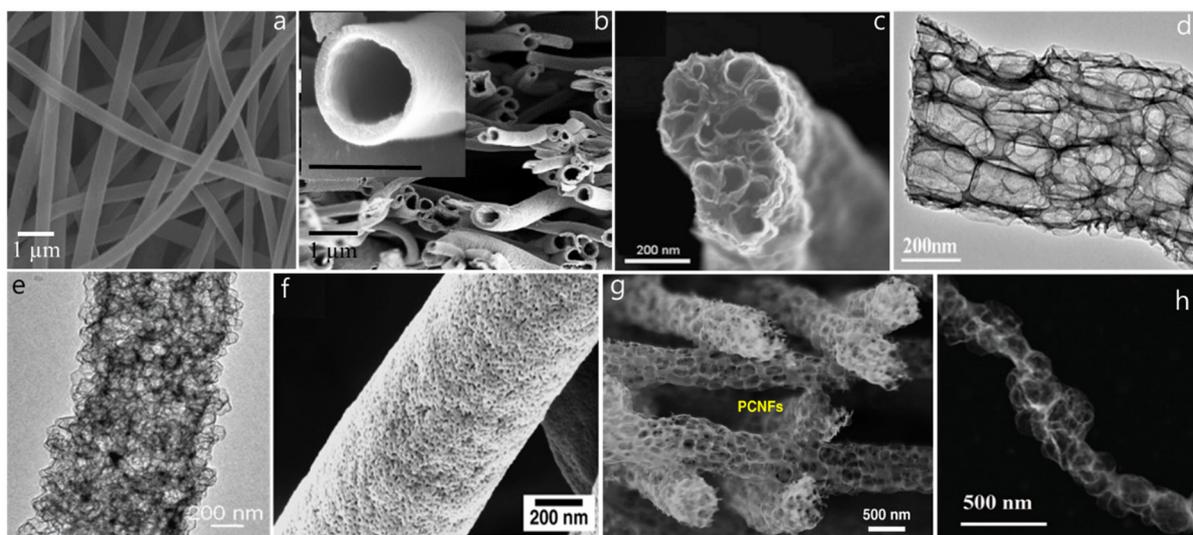


Figure 3. (a) SEM image of a CNF obtained by electrospinning PAN. (b) Field emission electron microscopy (FESEM) image of a hollow carbon nanofiber (HCNF) prepared by the coaxial electrospinning of PAN/PMMA (scale of the inset is 500 nm). (c) FESEM image of a porous carbon nanofiber (PCNF) prepared by electrospinning a PAN/PMMA blend and treated at 2800 °C. (d) Transmission electron microscopy (TEM) image of macroporous CNFs obtained by etching silica-reinforced carbon nanofibers with encapsulated antimony (Sb) nanoparticles ($\text{SiO}_2/\text{Sb@CNF}$) composite with an aqueous hydrogen fluoride (HF) solution. (e) TEM image of an N-doped PCNF prepared by a metal-organic framework (MOF)-based approach. (f) FESEM image of a PCNF by electrospinning a poly(acrylonitrile-block-methyl methacrylate) polymer. (g) SEM image of a triple-doped B-N-F sponge-like PCNF. (h) TEM image of an N-doped necklace-like HCNF. (a) Reprinted with permission [101], Copyright Elsevier 2019. (b) Reprinted with permission [88], Copyright American Chemical Society 2020. (c) Reprinted with permission [100], Copyright 2007, Wiley-VCH. (d) Reprinted with permission [102], Copyright American Chemical Society 2018. (e) Reprinted with permission [44], Copyright The Royal Society of Chemistry 2017. (f) Reprinted with permission [91], Copyright Science Advances 2019 (g) Reprinted with permission [103], Copyright Springer Nature 2019. (h) Reprinted with permission [104], Copyright The Royal Society of Chemistry 2019.

A new strategy for the fabrication of highly porous nanofibers is the use of MOFs. MOFs, such as zeolitic imidazolate frameworks (ZIF-8, ZIF-67), can be directly developed in nanofibers during electrospinning or at later stages. MOFs are interesting new nanomaterials because of their unique and controllable features, such as their high porosity, large specific surface area, and variability in regard to metal ions and organic linkers; thus, they are attractive for a wide range of applications [105–109]. Chen et al. fabricated ZIF-8-mediated highly porous nitrogen-doped carbon nanofibers (Figure 3e) [44] that showed capacitances up to 307.2 F g^{-1} at a current density of 1 A g^{-1} ; additionally, this material retained a capacitance of 193.3 F g^{-1} at 50 A g^{-1} [44]. This high-value achievement was attributed to the superior Brunauer–Emmett–Teller (BET) surface area of the ZIF-8-induced porous ECNFs. The BET surface area was observed to be almost 50 times that of pure ECNFs. Therefore, compared to conventional materials, MOF-based nanomaterials usually exhibit a controllable porous architecture and pore volume along with an extraordinarily large surface area [108,110–114]. Furthermore, no additional template is required for promoting porosity. Heteroatom doping, which enhances the electronic properties of a material, needs additional chemicals and processes that may be complicated and hazardous. In the case of MOF-derived materials, the heteroatoms present in organic ligands, such as 2-methylimidazole, are directly doped and do not require additional chemicals or steps.

Another benefit of carbon nanofibers is their use as one of the constituents of nanocomposites or simply as light and conductive substrates for the growth of active materials. Different nanocarbons, such as graphene and CNTs, as well as many metal compounds, such as hydroxides, oxides, sulfides, and phosphides, in a number of shapes and sizes, have been engineered on CNFs to produce a variety of architectures. Qie et al. developed graphene-reinforced ECNFs that exhibited a specific capacitance of 183 F g^{-1} , approx-

imately 1.6 times higher than that of pristine CNFs [47]. Few reports have shown the growth of metal-based compounds on ECNFs as negative electrode materials for supercapacitors [115,116]. The optimal concentration of metal doping can be beneficial to obtain high capacitance without sacrificing EDLC behavior and the high conductivity of the carbon materials. Otherwise, the composite simply becomes a composite that demonstrates metal-dominated behavior, i.e., high Faradic activity and low stability [58].

Table 2. Precursors to obtain carbon fibers, their application, and properties.

S.N.	Polymer/Solvent	Fiber Diameter/Surface Area	Application	References
1	Polyacrylonitrile /dimethylformamide (PAN/DMF) with a metal precursor	200–500 nm/N/A	Energy storage	[59,88,117]
2	Coal, PAN/DMF	N/A	Energy storage	[118]
3	[PAN + PMMA + tin octoate]/DMF	N/A	Lithium-based batteries	[119]
4	PVP, cobalt nitrate [Co(NO ₃)] in water/ethanol	150 nm/N/A	Sodium ion batteries	[120]
5	ZIF-67, PAN/DMF	200 nm/338.37 m ² g ⁻¹	Li-S batteries	[121]
6	PAN, cobalt salt/DMF		Energy storage	[32]
7	PAN, terephthalic acid/DMF	400–600 nm/N/A	Electrochemical test	[122]
8	Pitch/DMF	Micrometer/N/A	Gas diffusion	[123]
9	Polyimide/dimethylacetamide (PI/DMAc)	Micrometer/N/A	n/a	[124]
10	Cellulose/acetone-dimethylacetamide	50–500 nm/N/A	Energy storage	[125]
11	PVP, ammonia borane/methanol	150 nm/145 m ² g ⁻¹	Lithium-ion batteries	[126]
12	Lignin, polyvinyl alcohol/distilled water (PVA/DW)	100 ± 23 nm/1670 m ² g ⁻¹	Energy storage	[127]
14	PAN, PVDF/DMF	200–300 nm/29 m ² g ⁻¹	CO ₂ adsorbents	[128]
15	Plant protein/acetic acid	413–900 nm/N/A	Energy storage	[129]

5. Challenges, Opportunities, and Future Directions

Generally, carbon fibers are brittle; therefore, it is very challenging to retain fibers in their free-standing and flexible state. There are some reports that show the successful fabrication of highly flexible carbon fibers, and they have been used to study electrochemical performance [130,131]. Tian et al. showed interconnected networks of carbon fibers that improved the integrity and buffered the volume expansion of an electrode, while contributing to its flexibility [132]. Similarly, Liu et al. [33] synthesized highly flexible electrospun-based carbon fibers from pitch using a crosslinking strategy. The as-designed product exhibited a capacitance of 170 F g⁻¹ at a current density of 1 A g⁻¹. Another challenge is to make a three-dimensional flexible network. As-spun membrane-derived carbon fibers are similar to a two-dimensional sheet composed of compacted fibers. In such a case, the modification of fibers by electrochemically active materials to achieve high performance can be limited to only the surface of exposed fibers, and the remaining internally located fibers of the membrane remain untouched [32]. Recently, the fabrication of three-dimensional foam-like carbonaceous structures has been reported [28,32,133]. For instance, electrospinning and subsequent post-processing (gas foaming) result in a three-dimensional network structure. Tiwari et al. [28,32] recently demonstrated a three-dimensional carbonaceous porous network that exhibited high capacitances up to 205 F g⁻¹ at a current density of 1 A g⁻¹. The PAN nanofibrous mats were first fabricated in a three-dimensional shape by sodium borohydride-mediated hydrolysis, causing hydrogen gas to become trapped into the fibrous network. Later, these were carbonized to obtain carbon fibers. Current challenges

can become opportunities in the future. The synthesis of highly flexible carbon nanofibers with a high capacitance that work over a wide range of potentials can be a future opportunity. Recently, MOFs have become promising materials for the development of porous and highly branched crosslinked networks [134,135]. In this context, the integration of MOF-derived networks into porous and hollow carbon nanofibers with negative electrode materials can overcome the challenges associated with pure carbon nanofibers, such as their brittleness, inflexibility, low capacitance, and low energy density. It is expected that the highly flexible free-standing configuration of ECNF membranes will be an option for developing the next generation of flexible energy storage devices.

6. Conclusions

In this review, we reported the ECNF-based negative electrode materials used in supercapacitors. Among the many carbonaceous materials, ECNFs have many advantages, such as the possibility of developing free-standing materials and their ability to accommodate other active compounds to achieve higher performances. Strategies to obtain higher capacitance by modifying ECNFs without disturbing the EDLC behavior of carbon nanofibers were discussed in this report. By reviewing the literature and providing critical analysis, it was found that the creation of highly porous networks along with metal doping and heteroatom doping are promising strategies for developing anode materials with high capacitance values. We expect that the shortcomings of pure ECNFs in energy storage can be overcome by the use of secondary techniques and strategies. Overall, this review explores the negative electrode materials used thus far and provides insight for the further development of high-performance supercapacitors to use in next-generation devices.

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