Article

A review of electrospun carbon nanofiber-based negative electrode materials for supercapacitors

Arjun Prasad Tiwari[a,1,*]**, Tanka Mukhiya**[b, c, 1]**, Alagan Muthurasu**[c]**, Minju Lee**[c]**, Kisan Chhetri**[c]**, Bipeen Dahal**[c,d]**, Prakash Chandra Lohani**[c] **and Hak Yong Kim** [c*]

[a] Carbon Nano Convergence Technology for Next generation Engineers (CNN), Jeonju 561-756, Republic of Korea

[b] Department of Chemistry, Bhaktapur Multiple Campus, Tribhuvan University, Nepal

[c] Department of Nano Convergence Engineering, Jeonbuk National University, Jeonju 561-756, Republic of Korea

[d] Central Department of Chemistry, Tribhuvan University, Nepal

* Correspondence: author: tiwariarjuna@gmail.com (A.P.Tiwari) and dragon4875@gmail.com (H.Y. Kim)

[1]These authors contributed equally.

Abstract: The development of smart negative electrode materials with high capacitance for use in supercapacitors remains challenging. Although there have been several types of electrode materials with high capacitance used in energy storage, 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 as-formed 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 energy density on their own. To this end, several attempts have been made to improve these characteristics. In this review, we introduce negative electrode materials that have been developed. Moreover, this review places special attention to the advances of electrospun nanofiber-based negative electrode materials and their limitations. Based on the above information, 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

1. Introduction

Electrical energy has been an indispensable aspect of human civilization. It is essential to run our day-to-day activities, develop infrastructures, drive the economy and discover materials and technologies for human welfare. 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 major contributor of CO_2 emissions that are responsible for life-threatening global warming. Moreover, fossil fuel sources are rapidly being exhausted and they are inherently nonrenewable [4]. The above facts demonstrates 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 road-

blocks in the roadmap of driving our civilization toward 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 (∽300 W h kg^{-1}) have tremendously contributed to this field and have been recognized with the Nobel prize in Chemistry 2019; however, these 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 (∽10^5 W kg^{-1}) and long operating life (>10^6 charge-discharge cycles), have appeared to be 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 storing 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 by mainly 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 high 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 eco-friendly materials, availability of simple and fast fabrication processes, demonstration of multifunctional use and capacity for mass production are parameters that always lie 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 supercapacitor device. A battery has a high energy density but a low power density, while a supercapacitor is 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 windows of the device and the capacitance, as indicated by the formula, Energy density (E)=1/2CV^2, where C is the capacitance and V is the working potential window. This demand further focuses on developing devices with high capacitance that work over a wide potential range. Several thousands of works 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 [28-31] (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 [32-34]. 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 high surface area and outstanding conductivity, compared to metal-based electrodes. The major carbon materials are activated carbon (AC) [35,36], carbon nanotubes (CNTs) [37,38], graphene [39], carbon cloth (CC) [40], electrospun carbon nanofibers [41,42], porous carbons [43-45] 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.	ZIF-8NPC	3 M KOH	$190.0 \ F \ g^{-1}$	$1 \ A \ g^{-1}$	[44]
2.	3D-BN-CNF-F900	2 M KOH	$295.0 \ F \ g^{-1}$	$0.5 \ A \ g^{-1}$	[41]
3.	rGO-CNF hybrid (1:1)	6 M KOH	$316.5 \ F \ g^{-1}$	$0.25 \ A \ g^{-1}$	[42]
4.	ZIF-7/glucose composite-derived carbon-L-950	6 M KOH	$228.0 \ F \ g^{-1}$	$0.1 \ A \ g^{-1}$	[45]
5.	CNT@Gr-CNF-5	6 M KOH	$521.5 \ F \ g^{-1}$	$0.25 \ A \ g^{-1}$	[38]
6.	G/CNT/Fe_2O_3-150	1 M Li_2SO_4	$258.0 \ F \ g^{-1}$	$1 \ A \ g^{-1}$	[46]
7.	V_2O_5/VACNT composites	1 M Na_2SO_4	$284.0 \ F \ g^{-1}$	$2 \ A \ g^{-1}$	[21]
8.	PAN:PmAP-NCNF	6 M KOH	$347.5 \ F \ g^{-1}$	$0.5 \ mA \ cm^{-2}$	[47]
9.	NCNF-900@Ppy	6 M KOH	$202.0 \ F \ g^{-1}$	$1 \ A \ g^{-1}$	[48]

10	Porous CNF-3	6 M KOH	314.0 F g^{-1}	0.5 A g^{-1}	[49]
11.	HPCT (hierarchical porous carbon nanotube)	6 M KOH	386.2 F g^{-1}	0.1 A g^{-1}	[50]
13.	CNT@CNF	6 M KOH	464.2 F g^{-1}	0.5 A g^{-1}	[51]
14.	Porous CNFs	6 M KOH	362.0 F g^{-1}	0.2 A g^{-1}	[52]
15.	Activated CNF	6 M KOH	156.0 F g^{-1}	0.5 A g^{-1}	[31]
16.	CNF/graphene	6 M KOH	183.0 F g^{-1}	1 A g^{-1}	[53]
17.	CNT@Graphene	6 M KOH	401.0 F g^{-1}	1 A g^{-1}	[30]
19.	CNF-40 (PF:PAN = 40:60)	1 M H$_2$SO$_4$	271.6 F g^{-1}	0.5 A g^{-1}	[54]
20.	Nitrogen-doped hollow activated carbon nanofibers (HACNFs)	6 M KOH	197.0 F g^{-1}	0.2 A g^{-1}	[55]
21.	80:20 PAN/PAN-co-PB derived CNF	2 M KOH	172.0 F g^{-1}	1 A g^{-1}	[29]
22.	Three-dimensional porous CNFs (P@3D-CNF)	2 M KOH	205.5 F g^{-1}	1 A g^{-1}	[28]
23.	Amorphous cobalt phosphate/carbon (CoPi/C)	2 M KOH	606.1 F g^{-1} (2.15 F cm^{-2})	1 A g^{-1} (4 mA cm^{-2})	[56]
24	Electrodeposited MoOx film	1 M H$_2$SO$_4$	507.0 F g^{-1}	1 A g^{-1}	[24]
25	3D Ti3C2 aerogel	1 M KOH	1012.0 mF cm^{-2}	2 mV s^{-1}	[18]
26	Carbon-coated TiN	1 M KOH	167.0 F g^{-1}	1 A g^{-1}	[19]
27	Ta-Cu$_7$S$_4$	1 M KOH	675.0 F g^{-1}	1 A g^{-1}	[20]
28	Vanadium oxides (VOx)	5 M LiCl	1652.3 F g^{-1}	2 mA cm^{-2}	[22]
29	MoO$_2$/MoS$_2$	1 M Na$_2$SO$_4$	433.3 F g^{-1}	5 mV s^{-1}	[23]
30	FeP nanotubes	1 M LiCl	149.11 F g^{-1}	1 mA cm^{-2}	[27]

3. Carbon-based negative electrode materials

The conventional electrode material for electrical double layer capacitors (EDLCs) is porous AC with a high specific surface area of ~2500 $m^2 g^{-1}$, which delivers capacitances of 200 F g^{-1} and 100 F g^{-1} in aqueous and organic electrolytes, respectively [35,57]. Graphene has been considered a promising material as a negative electrode [58]. 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 [59]. 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 powered form and tendency to quickly aggregate. Self-supported electrode materials are necessary to make a device function independently. CC holds promise as a self-supporting highly conductive substrate with high strength and flexibility. However, CC by itself has an extremely low capacitance due to its low surface area (<10 $m^2 g^{-1}$) 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 [60]. 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 [61,62]. Moreover, the functionalization of carbon cloth materials also improves their performance by increasing conductivity and accommodating other double layer capacitance-contributing materials [63-65]. Porous nitrogen-doped carbon cloth exhibits a capacitance of 190 F g^{-1} [66]. Heterodoping a mesoporous and functionalized CC can further increase the capacitance while exhibiting a wide working potential [56]. Tiwari et al. [56] 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. This capacitance value is the highest among modified CC-based electrodes. 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 showed 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 is 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 [67].
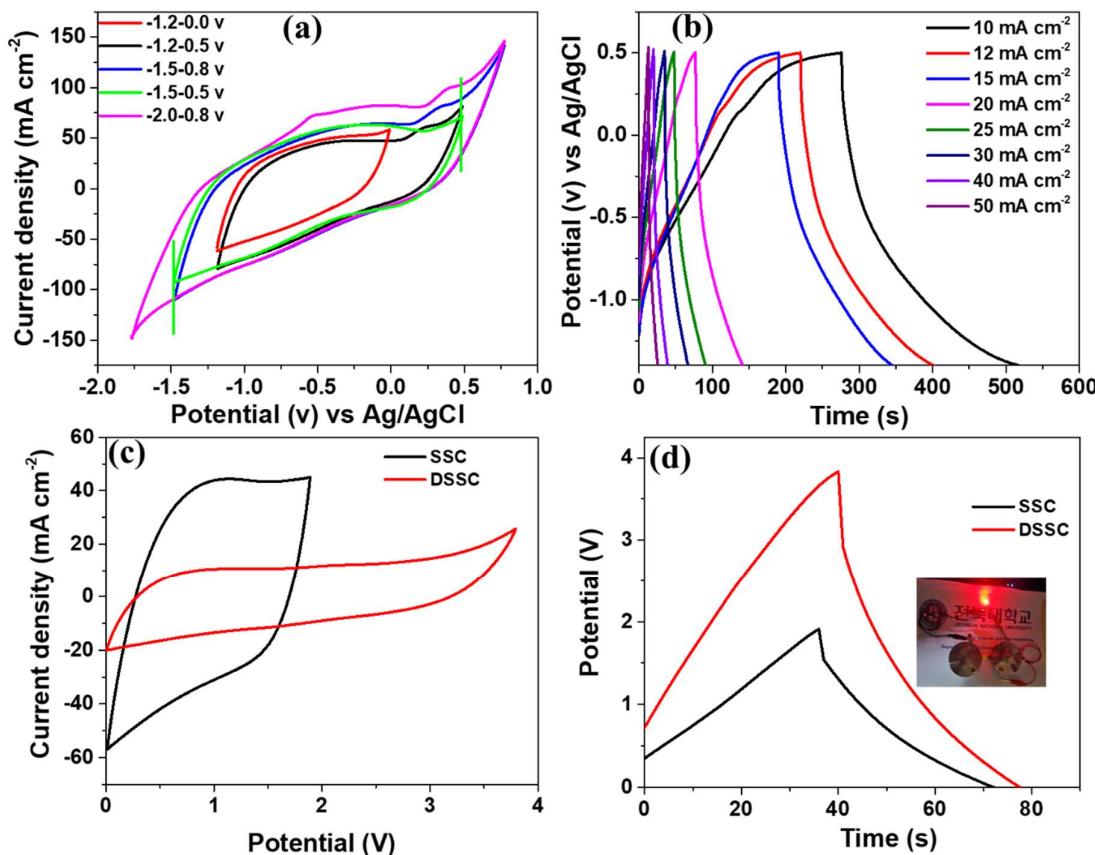
Figure 1. CV curves of a-PC@CoPi-CC8 within different potential windows at 50 mV s⁻¹ (a), GCD curves of the same sample at different current densities at potential ranges from -1.4 to 0.5 (b). CV profiles of a symmetric supercapacitor (SSC) and a double SSC (DSSC) collected at 50 mV s⁻¹ (c), and GCD curves of the SSC and DSSC devices collected at 20 mA cm⁻² (d). Inset is the image of a red LED powered by two SSCs in series. The supercapacitor devices were charged for approximately 40 s before the LED tests. Reprinted with permission [56].

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 [37,57,58]. Most importantly, electrospun fibers can be produced with a simple machine in a laboratory setting, unlike the need for a company setup to produce carbon cloth. CNFs can be fabricated by the cost-effective and convenient electrospinning of organic polymers followed by carbonization [68-70]. 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. In 1887, C. V. Boys showed that fibers could be produced from a viscoelastic liquid in the presence of an external electric field [71]. In 1902, J. F. Cooley and J. Martin filed patents for a prototype setup for electrospinning [69]. In 1964-69, Geoffery 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 [72-74]. 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 [75-79]. 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 electrospinning of a polymer solution, along with the morphology, structure and functionality of the nanofibrous material are determined by the nature of the polymer, solvent and processing parameters. Currently, a large number of

natural and synthetic polymers have been successfully reported for the fabrication of nanofibers by electrospinning [69]. 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; and 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.
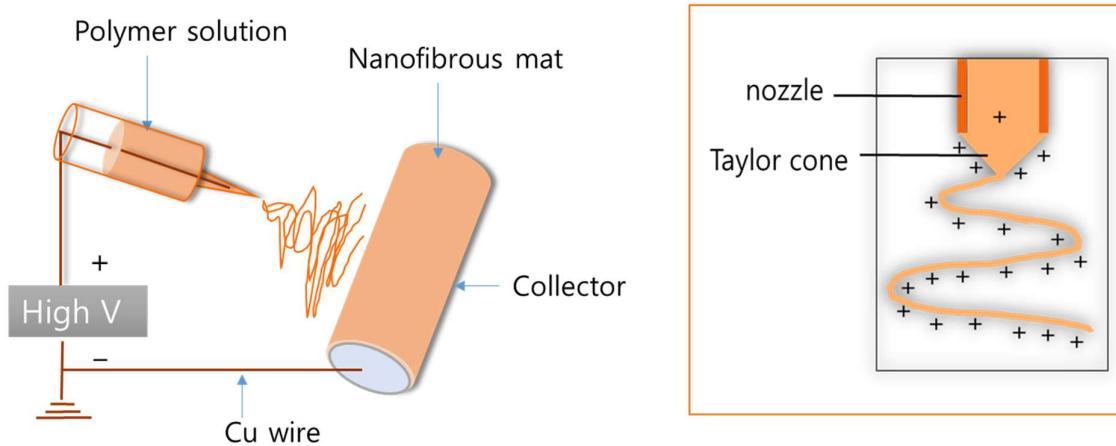
Figure 2. Schematic representing the simple electrospinning process.

CNF sheets consist of very long nonwoven 1D carbon nanofibers that form 2D sheets that can be modified into 3D sheets. The large specific surface area, chemical stability, light weight, good conductivity, easy accessibility, and environmentally friendly nature of CNFs are attractive features. In addition to these features, 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 high specific surface area, and diverse functionalities can be fabricated [80-85]. (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 [86,87]. ECNF sheets as current collectors instead of heavy metals, such as nickel foam, significantly reduce the weight of electrodes [88,89]. (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 freestanding electrodes [90,91]. (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 [92,93].

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 [57,58]. The postmodification approaches for increasing capacitance are more or less similar to those of CC.

The most commonly used polymer to synthesize carbon nanofibers is polyacrylonitrile (PAN) due to its high carbon yield compared to other polymers; however, there are other polymers that 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 for far 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 low 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, a high and controllable porosity, and 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 [78]. 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) [81]. Electrospinning PAN/PMMA blends with different ratios produces multiporous nanofibers (Figure 3c) [94].
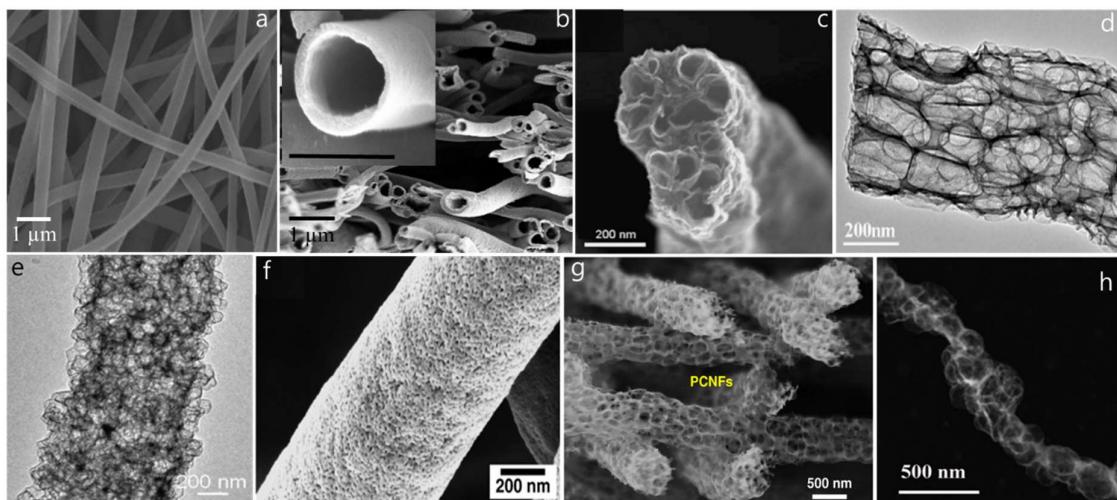

Figure 3. (a) SEM image of a CNF obtained by electrospinning PAN. (b) FESEM image of an HCNF prepared by the coaxial electrospinning of PAN/PMMA (scale of the inset is 500 nm). (c) FESEM image of a PCNF prepared by electrospinning a PAN/PMMA blend and treated at 2800 °C. (d) TEM image of macroporous CNFs obtained by etching a SiO$_2$/Sb@CNF composite with an aqueous 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.

The approach of using block copolymer-based precursors is significant for controlling porosity of the resulting material and may revolutionize the synthesis of PCNFs [84]. Zhou et al synthesized dual-doped porous carbon nanofibers (PCNFs) with well-controlled bimodal pores, namely, mesopores (10 nm) and micropores (0.5 nm), by electrospinning poly(acrylonitrile-block-methyl methacrylate) (Figure 3f) [84]. 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-micro pores and an ultrahigh porosity (>80%) and outstanding conductivity (980 S cm^{-1}), while being triple doped with B-F-N (Figure 3g) [97]. Yang et prepared necklace-like hollow carbon nanofibrous materials with an abundance of micro/meso/micropores and an ultrahigh content of doped N (Figure 3h) [98]. 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 SiO$_2$- and Sb-entrapped nanofibers by electrospinning SbCl$_3$, PV, and tetraethylorthosilicate (TEOS). After carbonization and etching with HF, a highly porous carbon nanofibrous structure was obtained (Figure 3d) [96]. They later used this electrode as a highly stable electrode for Li batteries.

A new strategy for the fabrication of highly porous nanofibers is the use of metal-organic frameworks (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 [99-103]. Chen et al fabricated ZIF-8-mediated highly porous nitrogen-doped carbon nanofibers (Figure 3e) [43] 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} [43]. The reason behind this high-value achievement was attributed to the superior 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 high surface area [104-109]. 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 beauty 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}, approximately 1.6 times higher than that of pristine CNFs [53]. Few reports have shown the growth of metal-based compounds on ECNFs as negative electrode materials for supercapacitors

[110,111]. 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 [56].

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

S.N.	Polymer/solvent	Fiber diameter/surface area	Application	References
1	PAN/(DMF) with a metal precursor	200-500 nm/n/a	Energy storage	[57,81] [112]
2	Coal, PAN/DMF	n/a	Energy storage	[113]
3	[PAN + PMMA + tin octoate]/DMF	n/a	Lithium-based batteries	[114]
4	PVP, $Co(NO_3)$ water/ethanol	150 nm/n/a	Sodium ion batteries	[115]
5	ZIF-67, PAN/DMF	200 nm/338.37 m^2 g^{-1}	Li–S batteries	[116]
6	PAN, cobalt salt/DMF		Energy storage	[58]
7	PAN, terephthalic acid/DMF	400–600 nm/n/a	Electrochemical test	[117]
8	Pitch/DMF	Micrometer/n/a	Gas diffusion	[118]
9	Polyimide/DMAc	Micrometer/n/a	n/a	[119]
10	Cellulose/acetone-DMAc	50-500 nm/n/a	Energy storage	[120]
11	PVP, ammonia borane/methanol	150 nm/145 m^2 g^{-1}	Lithium-ion batteries	[121]
12	Lignin, PVA/DW	100±23 nm/1670 m^2 g^{-1}	Energy storage	[122]
14	PAN, PVDF/DMF	200-300 nm/29 m^2 g^{-1}	CO_2 adsorbents	[123]
15	Plant protein/acetic acid	413-900 nm/n/a	Energy storage	[124]

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 [125,126]. 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 [127]. Similarly, Liu et al. [32] 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 [58]. Recently, the fabrication of three-dimensional foam-like carbonaceous structures have been reported [28,58,128]. For instance, electrospinning and subsequent post-processing (gas foaming) result in a three-dimensional network structure. Tiwari et al. [28,58] recently showed 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 always later become opportunities. The synthesis of highly flexible carbon nanofibers with a high capacitance that work over a wide range of potentials can be a future choice. Recently, MOFs have become promising materials for the development of porous and highly branched crosslinked networks [129,130]. In this background, 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 an ECNF membrane will be the choice for developing the next generation of flexible energy storage devices.

6. Conclusion

In this review, we compiled electrospun carbon nanofiber-based materials that are mainly used in supercapacitors. Carbon-based materials have been considered the current requirement for negative electrode materials used in supercapacitor devices. Among them, ECNFs have many advantages, such as the possibility of developing free-standing materials and their accommodation of other active compounds to achieve higher performances than their corresponding carbon material counterparts. Strategies to obtain higher capacitance by modifying ECNFs without disturbing the EDLC behavior of carbon nanofibers was discussed in this report. By reviewing the literature and providing a critical analysis, it was found that the creation of highly porous networks along with the combination of metal derivatives and heteroatom doping can be a promising strategy to develop 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.

References

1. Gür, T.M. Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage. *Energy & Environmental Science* **2018**, *11*, 2696-2767, doi:10.1039/C8EE01419A.
2. Agency, I.E. *World Energy Outlook 2018*; 2018; doi:https://doi.org/10.1787/weo-2018-en.
3. Jin, H.; Li, J.; Yuan, Y.; Wang, J.; Lu, J.; Wang, S. Recent Progress in Biomass-Derived Electrode Materials for High Volumetric Performance Supercapacitors. *Advanced Energy Materials* **2018**, *8*, 1801007, doi:10.1002/aenm.201801007.
4. Capellán-Pérez, I.; Arto, I.; Polanco-Martínez, J.M.; González-Eguino, M.; Neumann, M.B. Likelihood of climate change pathways under uncertainty on fossil fuel resource availability. *Energy & Environmental Science* **2016**, *9*, 2482-2496, doi:10.1039/C6EE01008C.
5. Khan, N.; Dilshad, S.; Khalid, R.; Kalair, A.R.; Abas, N. Review of energy storage and transportation of energy. *Energy Storage* **2019**, *1*, e49, doi:10.1002/est2.49.
6. Palacín, M.R.; de Guibert, A. Why do batteries fail? *Science* **2016**, *351*, 1253292, doi:10.1126/science.1253292.
7. El Kharbachi, A.; Zavorotynska, O.; Latroche, M.; Cuevas, F.; Yartys, V.; Fichtner, M. Exploits, advances and challenges benefiting beyond Li-ion battery technologies. *Journal of Alloys and Compounds* **2020**, *817*, 153261, doi:https://doi.org/10.1016/j.jallcom.2019.153261.
8. Simon, P.; Gogotsi, Y.; Dunn, B. Where Do Batteries End and Supercapacitors Begin? *Science* **2014**, *343*, 1210, doi:10.1126/science.1249625.

9.   Zhou, Y.; Wang, C.-H.; Lu, W.; Dai, L. Recent Advances in Fiber-Shaped Supercapacitors and Lithium-Ion Batteries. *Advanced Materials* **2020**, *32*, 1902779, doi:10.1002/adma.201902779.

10. Gou, Q.; Zhao, S.; Wang, J.; Li, M.; Xue, J. Recent Advances on Boosting the Cell Voltage of Aqueous Supercapacitors. *Nano-Micro Letters* **2020**, *12*, 98, doi:10.1007/s40820-020-00430-4.

11. Bi, Z.; Kong, Q.; Cao, Y.; Sun, G.; Su, F.; Wei, X.; Li, X.; Ahmad, A.; Xie, L.; Chen, C.-M. Biomass-derived porous carbon materials with different dimensions for supercapacitor electrodes: a review. *Journal of Materials Chemistry A* **2019**, *7*, 16028-16045, doi:10.1039/C9TA04436A.

12. Merlet, C.; Rotenberg, B.; Madden, P.A.; Taberna, P.-L.; Simon, P.; Gogotsi, Y.; Salanne, M. On the molecular origin of supercapacitance in nanoporous carbon electrodes. *Nature Materials* **2012**, *11*, 306-310, doi:10.1038/nmat3260.

13. Yu, Z.; Tetard, L.; Zhai, L.; Thomas, J. Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy & Environmental Science* **2015**, *8*, 702-730, doi:10.1039/C4EE03229B.

14. Chen, H.; Hu, L.; Chen, M.; Yan, Y.; Wu, L. Nickel–cobalt layered double hydroxide nanosheets for high-performance supercapacitor electrode materials. *Advanced Functional Materials* **2014**, *24*, 934-942.

15. Liang, H.; Jia, H.; Lin, T.; Wang, Z.; Li, C.; Chen, S.; Qi, J.; Cao, J.; Fei, W.; Feng, J. Oxygen-vacancy-rich nickel-cobalt layered double hydroxide electrode for high-performance supercapacitors. *Journal of Colloid and Interface Science* **2019**, *554*, 59-65, doi:https://doi.org/10.1016/j.jcis.2019.06.095.

16. Yang, J.; Yu, C.; Hu, C.; Wang, M.; Li, S.; Huang, H.; Bustillo, K.; Han, X.; Zhao, C.; Guo, W., et al. Surface-Confined Fabrication of Ultrathin Nickel Cobalt-Layered Double Hydroxide Nanosheets for High-Performance Supercapacitors. *Advanced Functional Materials* **2018**, *28*, 1803272, doi:https://doi.org/10.1002/adfm.201803272.

17. Wei, Z.; Yuan, J.; Tang, S.; Wu, D.; Wu, L. Porous nanorods of nickel–cobalt double hydroxide prepared by electrochemical co-deposition for high-performance supercapacitors. *Journal of Colloid and Interface Science* **2019**, *542*, 15-22, doi:https://doi.org/10.1016/j.jcis.2019.01.114.

18. Li, L.; Zhang, M.; Zhang, X.; Zhang, Z. New Ti3C2 aerogel as promising negative electrode materials for asymmetric supercapacitors. *Journal of Power Sources* **2017**, *364*, 234-241, doi:https://doi.org/10.1016/j.jpowsour.2017.08.029.

19. Grote, F.; Zhao, H.; Lei, Y. Self-supported carbon coated TiN nanotube arrays: innovative carbon coating leads to an improved cycling ability for supercapacitor applications. *Journal of Materials Chemistry A* **2015**, *3*, 3465-3470, doi:10.1039/C4TA05905K.

20. Han, X.; Zhang, D.; Qin, Y.; Kong, X.; Zhang, F.; Lei, X. Construction of Ta-Cu7S4 negative electrode for high-performance all-solid-state asymmetric supercapacitor. *Chemical Engineering Journal* **2021**, *403*, 126471, doi:https://doi.org/10.1016/j.cej.2020.126471.

21. Sun, G.; Ren, H.; Shi, Z.; Zhang, L.; Wang, Z.; Zhan, K.; Yan, Y.; Yang, J.; Zhao, B. V2O5/vertically-aligned carbon nanotubes as negative electrode for asymmetric supercapacitor in neutral aqueous electrolyte. *Journal of Colloid and Interface Science* **2021**, *588*, 847-856, doi:https://doi.org/10.1016/j.jcis.2020.11.126.

22. Zheng, K.; Zeng, Y.; Liu, S.; Zeng, C.; Tong, Y.; Zheng, Z.; Zhu, T.; Lu, X. Valence and surface modulated vanadium oxide nanowires as new high-energy and durable negative electrode for flexible asymmetric supercapacitors. *Energy Storage Materials* **2019**, *22*, 410-417.

23. Zhang, T.; Kong, L.-B.; Liu, M.-C.; Dai, Y.-H.; Yan, K.; Hu, B.; Luo, Y.-C.; Kang, L. Design and preparation of MoO2/MoS2 as negative electrode materials for supercapacitors. *Materials & Design* **2016**, *112*, 88-96, doi:https://doi.org/10.1016/j.matdes.2016.09.054.

24. Upadhyay, K.K.; Nguyen, T.; Silva, T.M.; Carmezim, M.J.; Montemor, M.F. Electrodeposited MoOx films as negative electrode materials for redox supercapacitors. *Electrochimica Acta* **2017**, *225*, 19-28.

25. Long, C.; Wei, T.; Yan, J.; Jiang, L.; Fan, Z. Supercapacitors based on graphene-supported iron nanosheets as negative electrode materials. *ACS nano* **2013**, *7*, 11325-11332.

26. Luo, J.; Zheng, Z.; Kumamoto, A.; Unah, W.I.; Yan, S.; Ikuhara, Y.H.; Xiang, X.; Zu, X.; Zhou, W. PEDOT coated iron phosphide nanorod arrays as high-performance supercapacitor negative electrodes. *Chemical Communications* **2018**, *54*, 794-797.

27. Liang, B.; Zheng, Z.; Retana, M.; Lu, K.; Wood, T.; Ai, Y.; Zu, X.; Zhou, W. Synthesis of FeP nanotube arrays as negative electrode for solid-state asymmetric supercapacitor. *Nanotechnology* **2019**, *30*, 295401, doi:10.1088/1361-6528/ab0620.

28. Tiwari, A.P.; Chhetri, K.; Kim, H.; Ji, S.; Chae, S.-H.; Kim, T.; Kim, H.Y. Self-assembled polypyrrole hierarchical porous networks as the cathode and porous three dimensional carbonaceous networks as the anode materials for asymmetric supercapacitor. *Journal of Energy Storage* **2021**, *33*, 102080, doi:https://doi.org/10.1016/j.est.2020.102080.

29. Hsu, Y.-H.; Lai, C.-C.; Ho, C.-L.; Lo, C.-T. Preparation of interconnected carbon nanofibers as electrodes for supercapacitors. *Electrochimica Acta* **2014**, *127*, 369-376, doi:https://doi.org/10.1016/j.electacta.2014.02.060.

30. Yang, Z.-Y.; Zhao, Y.-F.; Xiao, Q.-Q.; Zhang, Y.-X.; Jing, L.; Yan, Y.-M.; Sun, K.-N. Controllable Growth of CNTs on Graphene as High-Performance Electrode Material for Supercapacitors. *ACS Applied Materials & Interfaces* **2014**, *6*, 8497-8504, doi:10.1021/am501362g.

31.   Zhi, M.; Liu, S.; Hong, Z.; Wu, N. Electrospun activated carbon nanofibers for supercapacitor electrodes. *RSC Advances* **2014**, *4*, 43619-43623, doi:10.1039/C4RA05512H.

32.   Tian, X.; He, Y.; Song, Y.; Yang, T.; Li, X.; Liu, Z. Flexible Cross-Linked Electrospun Carbon Nanofiber Mats Derived from Pitch as Dual-Functional Materials for Supercapacitors. *Energy & Fuels* **2020**, *34*, 14975-14985, doi:10.1021/acs.energyfuels.0c02847.

33.   Zheng, S.; Li, Q.; Xue, H.; Pang, H.; Xu, Q. A highly alkaline-stable metal oxide@ metal–organic framework composite for high-performance electrochemical energy storage. *National Science Review* **2020**, *7*, 305-314.

34.   Siraj, N.; Macchi, S.; Berry, B.; Viswanathan, T. Metal-Free Carbon-Based Supercapacitors—A Comprehensive Review. *Electrochem* **2020**, *1*, 410-438.

35.   Frackowiak, E. Carbon materials for supercapacitor application. *Physical Chemistry Chemical Physics* **2007**, *9*, 1774-1785, doi:10.1039/B618139M.

36.   Denmark, I.; Macchi, S.; Watanabe, F.; Viswanathan, T.; Siraj, N. Effect of KOH on the Energy Storage Performance of Molasses-Based Phosphorus and Nitrogen Co-Doped Carbon. *Electrochem* **2021**, *2*, 29-40.

37.   Wang, L.; Zhang, G.; Zhang, X.; Shi, H.; Zeng, W.; Zhang, H.; Liu, Q.; Li, C.; Liu, Q.; Duan, H. Porous ultrathin carbon nanobubbles formed carbon nanofiber webs for high-performance flexible supercapacitors. *Journal of Materials Chemistry A* **2017**, *5*, 14801-14810, doi:10.1039/C7TA03445H.

38.   Kshetri, T.; Tran, D.T.; Nguyen, D.C.; Kim, N.H.; Lau, K.-t.; Lee, J.H. Ternary graphene-carbon nanofibers-carbon nanotubes structure for hybrid supercapacitor. *Chemical Engineering Journal* **2020**, *380*, 122543, doi:https://doi.org/10.1016/j.cej.2019.122543.

39.   Song, B.; Wu, F.; Zhu, Y.; Hou, Z.; Moon, K.-s.; Wong, C.-P. Effect of polymer binders on graphene-based free-standing electrodes for supercapacitors. *Electrochimica Acta* **2018**, *267*, 213-221.

40.   Zhang, S.; Dai, P.; Liu, H.; Yan, L.; Song, H.; Liu, D.; Zhao, X. Metal-organic framework derived porous flakes of cobalt chalcogenides (CoX, X = O, S, Se and Te) rooted in carbon fibers as flexible electrode materials for pseudocapacitive energy storage. *Electrochimica Acta* **2021**, *369*, 137681, doi:https://doi.org/10.1016/j.electacta.2020.137681.

41.   Dahal, B.; Mukhiya, T.; Ojha, G.P.; Muthurasu, A.; Chae, S.-H.; Kim, T.; Kang, D.; Kim, H.Y. In-built fabrication of MOF assimilated B/N co-doped 3D porous carbon nanofiber network as a binder-free electrode for supercapacitors. *Electrochimica Acta* **2019**, *301*, 209-219, doi:https://doi.org/10.1016/j.electacta.2019.01.171.

42.   Kshetri, T.; Tran, D.T.; Singh, T.I.; Kim, N.H.; Lau, K.-t.; Lee, J.H. Effects of the composition of reduced graphene oxide/carbon nanofiber nanocomposite on charge storage behaviors. *Composites Part B: Engineering* **2019**, *178*, 107500, doi:https://doi.org/10.1016/j.compositesb.2019.107500.

43.   Chen, L.-F.; Lu, Y.; Yu, L.; Lou, X.W. Designed formation of hollow particle-based nitrogen-doped carbon nanofibers for high-performance supercapacitors. *Energy & Environmental Science* **2017**, *10*, 1777-1783, doi:10.1039/C7EE00488E.

44.   Chhetri, K.; Tiwari, A.P.; Dahal, B.; Ojha, G.P.; Mukhiya, T.; Lee, M.; Kim, T.; Chae, S.-H.; Muthurasu, A.; Kim, H.Y. A ZIF-8-derived nanoporous carbon nanocomposite wrapped with Co3O4-polyaniline as an efficient electrode material for an asymmetric supercapacitor. *Journal of Electroanalytical Chemistry* **2020**, *856*, 113670, doi:https://doi.org/10.1016/j.jelechem.2019.113670.

45.   Zhang, P.; Sun, F.; Shen, Z.; Cao, D. ZIF-derived porous carbon: a promising supercapacitor electrode material. *Journal of Materials Chemistry A* **2014**, *2*, 12873-12880, doi:10.1039/C4TA00475B.

46.   Ding, B.; Wu, X. Transition metal oxides anchored on graphene/carbon nanotubes conductive network as both the negative and positive electrodes for asymmetric supercapacitor. *Journal of Alloys and Compounds* **2020**, *842*, 155838, doi:https://doi.org/10.1016/j.jallcom.2020.155838.

47.   Choudhury, A.; Kim, J.-H.; Sinha Mahapatra, S.; Yang, K.-S.; Yang, D.-J. Nitrogen-Enriched Porous Carbon Nanofiber Mat as Efficient Flexible Electrode Material for Supercapacitors. *ACS Sustainable Chemistry & Engineering* **2017**, *5*, 2109-2118, doi:10.1021/acssuschemeng.6b02031.

48.   Chen, L.-F.; Zhang, X.-D.; Liang, H.-W.; Kong, M.; Guan, Q.-F.; Chen, P.; Wu, Z.-Y.; Yu, S.-H. Synthesis of Nitrogen-Doped Porous Carbon Nanofibers as an Efficient Electrode Material for Supercapacitors. *ACS Nano* **2012**, *6*, 7092-7102, doi:10.1021/nn302147s.

49.   Sheng, J.; Ma, C.; Ma, Y.; Zhang, H.; Wang, R.; Xie, Z.; Shi, J. Synthesis of microporous carbon nanofibers with high specific surface using tetraethyl orthosilicate template for supercapacitors. *International Journal of Hydrogen Energy* **2016**, *41*, 9383-9393, doi:https://doi.org/10.1016/j.ijhydene.2016.04.076.

50.   Zhu, T.; Zhou, J.; Li, Z.; Li, S.; Si, W.; Zhuo, S. Hierarchical porous and N-doped carbon nanotubes derived from polyaniline for electrode materials in supercapacitors. *Journal of Materials Chemistry A* **2014**, *2*, 12545-12551, doi:10.1039/C4TA01465K.

51.   Kshetri, T.; Thanh, T.D.; Singh, S.B.; Kim, N.H.; Lee, J.H. Hierarchical material of carbon nanotubes grown on carbon nanofibers for high performance electrochemical capacitor. *Chemical Engineering Journal* **2018**, *345*, 39-47, doi:https://doi.org/10.1016/j.cej.2018.03.143.

52.   Ma, C.; Li, Y.; Shi, J.; Song, Y.; Liu, L. High-performance supercapacitor electrodes based on porous flexible carbon nanofiber paper treated by surface chemical etching. *Chemical Engineering Journal* **2014**, *249*, 216-225, doi:https://doi.org/10.1016/j.cej.2014.03.083.

53.   Dong, Q.; Wang, G.; Hu, H.; Yang, J.; Qian, B.; Ling, Z.; Qiu, J. Ultrasound-assisted preparation of electrospun carbon nanofiber/graphene composite electrode for supercapacitors. *Journal of Power Sources* **2013**, *243*, 350-353, doi:https://doi.org/10.1016/j.jpowsour.2013.06.060.

54.   Ishita, I.; Singhal, R. Porous multi-channel carbon nanofiber electrodes using discarded polystyrene foam as sacrificial material for high-performance supercapacitors. *Journal of Applied Electrochemistry* **2020**, *50*, 809-820, doi:10.1007/s10800-020-01433-0.

55.   Xu, Q.; Yu, X.; Liang, Q.; Bai, Y.; Huang, Z.-H.; Kang, F. Nitrogen-doped hollow activated carbon nanofibers as high performance supercapacitor electrodes. *Journal of Electroanalytical Chemistry* **2015**, *739*, 84-88, doi:https://doi.org/10.1016/j.jelechem.2014.12.027.

56.   Kim, T.; Tiwari, A.P.; Chhetri, K.; Ojha, G.P.; Kim, H.; Chae, S.-H.; Dahal, B.; Lee, B.M.; Mukhiya, T.; Kim, H.Y. Phytic acid controlled in situ synthesis of amorphous cobalt phosphate/carbon composite as anode materials with a high mass loading for symmetrical supercapacitor: amorphization of the electrode to boost the energy density. *Nanoscale Advances* **2020**, *2*, 4918-4929, doi:10.1039/D0NA00670J.

57.   Mukhiya, T.; Dahal, B.; Ojha, G.P.; Kang, D.; Kim, T.; Chae, S.-H.; Muthurasu, A.; Kim, H.Y. Engineering nanohaired 3D cobalt hydroxide wheels in electrospun carbon nanofibers for high-performance supercapacitors. *Chemical Engineering Journal* **2019**, *361*, 1225-1234, doi:https://doi.org/10.1016/j.cej.2019.01.006.

58.   Tiwari, A.P.; Chae, S.-H.; Ojha, G.P.; Dahal, B.; Mukhiya, T.; Lee, M.; Chhetri, K.; Kim, T.; Kim, H.-Y. Three-dimensional porous carbonaceous network with in-situ entrapped metallic cobalt for supercapacitor application. *Journal of Colloid and Interface Science* **2019**, *553*, 622-630, doi:https://doi.org/10.1016/j.jcis.2019.06.070.

59.   Yu, M.; Huang, Y.; Li, C.; Zeng, Y.; Wang, W.; Li, Y.; Fang, P.; Lu, X.; Tong, Y. Building three-dimensional graphene frameworks for energy storage and catalysis. *Advanced Functional Materials* **2015**, *25*, 324-330.

60.   Dahal, B.; Chhetri, K.; Muthurasu, A.; Mukhiya, T.; Tiwari, A.P.; Gautam, J.; Lee, J.Y.; Chung, D.C.; Kim, H.Y. Biaxial Stretchability in High-Performance, All-Solid-State Supercapacitor with a Double-Layer Anode and a Faradic Cathode Based on Graphitic-2200 Knitted Carbon Fiber. *Advanced Energy Materials* **2021**, *11*, 2002961, doi:https://doi.org/10.1002/aenm.202002961.

61.   Wang, Y.; Song, Y.; Xia, Y. Electrochemical capacitors: mechanism, materials, systems, characterization and applications. *Chemical Society Reviews* **2016**, *45*, 5925-5950, doi:10.1039/C5CS00580A.

62.   Yue, Z.; Dunya, H.; Ashuri, M.; Kucuk, K.; Aryal, S.; Antonov, S.; Alabbad, B.; Segre, C.U.; Mandal, B.K. Synthesis of a very high specific surface area active carbon and its electrical double-layer capacitor properties in organic electrolytes. *ChemEngineering* **2020**, *4*, 43.

63.   He, X.; Mao, X.; Zhang, C.; Yang, W.; Zhou, Y.; Yang, Y.; Xu, J. Flexible binder-free hierarchical copper sulfide/carbon cloth hybrid supercapacitor electrodes and the application as negative electrodes in asymmetric supercapacitor. *Journal of Materials Science: Materials in Electronics* **2020**, *31*, 2145-2152, doi:10.1007/s10854-019-02737-4.

64.   Kang, M.; Zhou, S.; Zhang, J.; Ning, F.; Ma, C.; Qiu, Z. Facile fabrication of oxygen vacancy-rich α-Fe2O3 microspheres on carbon cloth as negative electrode for supercapacitors. *Electrochimica Acta* **2020**, *338*, 135820.

65.   Chen, L.-F.; Yu, Z.-Y.; Ma, X.; Li, Z.-Y.; Yu, S.-H. In situ hydrothermal growth of ferric oxides on carbon cloth for low-cost and scalable high-energy-density supercapacitors. *Nano Energy* **2014**, *9*, 345-354, doi:https://doi.org/10.1016/j.nanoen.2014.07.021.

66.   Liu, Y.-N.; Zhang, J.-N.; Wang, H.-T.; Kang, X.-H.; Bian, S.-W. Boosting the electrochemical performance of carbon cloth negative electrodes by constructing hierarchically porous nitrogen-doped carbon nanofiber layers for all-solid-state asymmetric supercapacitors. *Materials Chemistry Frontiers* **2019**, *3*, 25-31, doi:10.1039/C8QM00293B.

67.   Patiño, J.; López-Salas, N.; Gutiérrez, M.C.; Carriazo, D.; Ferrer, M.L.; del Monte, F. Phosphorus-doped carbon–carbon nanotube hierarchical monoliths as true three-dimensional electrodes in supercapacitor cells. *Journal of Materials Chemistry A* **2016**, *4*, 1251-1263.

68.   Zhang, B.; Kang, F.; Tarascon, J.-M.; Kim, J.-K. Recent advances in electrospun carbon nanofibers and their application in electrochemical energy storage. *Progress in Materials Science* **2016**, *76*, 319-380, doi:https://doi.org/10.1016/j.pmatsci.2015.08.002.

69.   Xue, J.; Wu, T.; Dai, Y.; Xia, Y. Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications. *Chemical Reviews* **2019**, *119*, 5298-5415, doi:10.1021/acs.chemrev.8b00593.

70.   Inagaki, M.; Yang, Y.; Kang, F. Carbon Nanofibers Prepared via Electrospinning. *Advanced Materials* **2012**, *24*, 2547-2566, doi:10.1002/adma.201104940.

71.   Boys, C.V. On the Production, Properties, and some suggested Uses of the Finest Threads. *Proceedings of the Physical Society of London* **1887**, *9*, 8-19, doi:10.1088/1478-7814/9/1/303.

72.   Taylor, G.I. Disintegration of water drops in an electric field. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1964**, *280*, 383-397, doi:10.1098/rspa.1964.0151.

73.   Taylor, G.I.; Van Dyke, M.D. The force exerted by an electric field on a long cylindrical conductor. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1966**, *291*, 145-158, doi:10.1098/rspa.1966.0085.

74.   Taylor, G.I.; Van Dyke, M.D. Electrically driven jets. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences* **1969**, *313*, 453-475, doi:10.1098/rspa.1969.0205.

75.   Dai, H.; Gong, J.; Kim, H.; Lee, D. A novel method for preparing ultra-fine alumina-borate oxide fibres via an electrospinning technique. *Nanotechnology* **2002**, *13*, 674-677, doi:10.1088/0957-4484/13/5/327.

76.   Loscertales, I.G.; Barrero, A.; Márquez, M.; Spretz, R.; Velarde-Ortiz, R.; Larsen, G. Electrically Forced Coaxial Nanojets for One-Step Hollow Nanofiber Design. *Journal of the American Chemical Society* **2004**, *126*, 5376-5377, doi:10.1021/ja049443j.

77.   Li, D.; Wang, Y.; Xia, Y. Electrospinning of Polymeric and Ceramic Nanofibers as Uniaxially Aligned Arrays. *Nano Letters* **2003**, *3*, 1167-1171, doi:10.1021/nl0344256.

78.   Li, D.; Xia, Y. Direct Fabrication of Composite and Ceramic Hollow Nanofibers by Electrospinning. *Nano Letters* **2004**, *4*, 933-938, doi:10.1021/nl049590f.

79.   Sun, Z.; Zussman, E.; Yarin, A.L.; Wendorff, J.H.; Greiner, A. Compound Core–Shell Polymer Nanofibers by Co-Electrospinning. *Advanced Materials* **2003**, *15*, 1929-1932, doi:https://doi.org/10.1002/adma.200305136.

80.   Liang, J.; Zhao, H.; Yue, L.; Fan, G.; Li, T.; Lu, S.; Chen, G.; Gao, S.; Asiri, Abdullah M.; Sun, X. Recent advances in electrospun nanofibers for supercapacitors. *Journal of Materials Chemistry A* **2020**, *8*, 16747-16789, doi:10.1039/D0TA05100D.

81.   Mukhiya, T.; Ojha, G.P.; Dahal, B.; Kim, T.; Chhetri, K.; Lee, M.; Chae, S.-H.; Muthurasu, A.; Tiwari, A.P.; Kim, H.Y. Designed Assembly of Porous Cobalt Oxide/Carbon Nanotentacles on Electrospun Hollow Carbon Nanofibers Network for Supercapacitor. *ACS Applied Energy Materials* **2020**, *3*, 3435-3444, doi:10.1021/acsaem.9b02501.

82.   Kaerkitcha, N.; Chuangchote, S.; Sagawa, T. Control of physical properties of carbon nanofibers obtained from coaxial electrospinning of PMMA and PAN with adjustable inner/outer nozzle-ends. *Nanoscale Research Letters* **2016**, *11*, 186, doi:10.1186/s11671-016-1416-7.

83.   El-Deen, A.G.; Barakat, N.A.M.; Khalil, K.A.; Kim, H.Y. Hollow carbon nanofibers as an effective electrode for brackish water desalination using the capacitive deionization process. *New Journal of Chemistry* **2014**, *38*, 198-205, doi:10.1039/C3NJ00576C.

84.   Zhou, Z.; Liu, T.; Khan, A.U.; Liu, G. Block copolymer–based porous carbon fibers. *Science Advances* **2019**, *5*, eaau6852, doi:10.1126/sciadv.aau6852.

85.   Wang, C.; Liu, C.; Li, J.; Sun, X.; Shen, J.; Han, W.; Wang, L. Electrospun metal–organic framework derived hierarchical carbon nanofibers with high performance for supercapacitors. *Chemical Communications* **2017**, *53*, 1751-1754, doi:10.1039/C6CC09832K.

86.   Nguyen, T.T.; Balamurugan, J.; Aravindan, V.; Kim, N.H.; Lee, J.H. Boosting the Energy Density of Flexible Solid-State Supercapacitors via Both Ternary NiV2Se4 and NiFe2Se4 Nanosheet Arrays. *Chemistry of Materials* **2019**, *31*, 4490-4504, doi:10.1021/acs.chemmater.9b01101.

87.   Li, W.-H.; Ding, K.; Tian, H.-R.; Yao, M.-S.; Nath, B.; Deng, W.-H.; Wang, Y.; Xu, G. Conductive Metal–Organic Framework Nanowire Array Electrodes for High-Performance Solid-State Supercapacitors. *Advanced Functional Materials* **2017**, *27*, 1702067, doi:10.1002/adfm.201702067.

88.   Peng, S.; Li, L.; Kong Yoong Lee, J.; Tian, L.; Srinivasan, M.; Adams, S.; Ramakrishna, S. Electrospun carbon nanofibers and their hybrid composites as advanced materials for energy conversion and storage. *Nano Energy* **2016**, *22*, 361-395, doi:https://doi.org/10.1016/j.nanoen.2016.02.001.

89.   Lai, C.-C.; Lo, C.-T. Preparation of Nanostructural Carbon Nanofibers and Their Electrochemical Performance for Supercapacitors. *Electrochimica Acta* **2015**, *183*, 85-93, doi:https://doi.org/10.1016/j.electacta.2015.02.143.

90.   Sari, F.N.I.; Ting, J.-M. Direct Growth of MoS2 Nanowalls on Carbon Nanofibers for Use in Supercapacitor. *Scientific Reports* **2017**, *7*, 5999, doi:10.1038/s41598-017-05805-z.

91.   Jiang, J.; Li, Y.; Liu, J.; Huang, X.; Yuan, C.; Lou, X.W. Recent Advances in Metal Oxide-based Electrode Architecture Design for Electrochemical Energy Storage. **2012**, *24*, 5166-5180, doi:10.1002/adma.201202146.

92.   Lin, T.; Chen, I.W.; Liu, F.; Yang, C.; Bi, H.; Xu, F.; Huang, F. Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage. *Science* **2015**, *350*, 1508, doi:10.1126/science.aab3798.

93.   Xue, Y.; Ding, Y.; Niu, J.; Xia, Z.; Roy, A.; Chen, H.; Qu, J.; Wang, Z.L.; Dai, L. Rationally designed graphene-nanotube 3D architectures with a seamless nodal junction for efficient energy conversion and storage. *Science Advances* **2015**, *1*, e1400198, doi:10.1126/sciadv.1400198.

94.   Kim, C.; Jeong, Y.I.; Ngoc, B.T.N.; Yang, K.S.; Kojima, M.; Kim, Y.A.; Endo, M.; Lee, J.-W. Synthesis and Characterization of Porous Carbon Nanofibers with Hollow Cores Through the Thermal Treatment of Electrospun Copolymeric Nanofiber Webs. *Small* **2007**, *3*, 91-95, doi:https://doi.org/10.1002/smll.200600243.

95.   Mukhiya, T.; Dahal, B.; Ojha, G.P.; Chhetri, K.; Lee, M.; Kim, T.; Chae, S.-H.; Tiwari, A.P.; Muthurasu, A.; Kim, H.Y. Silver nanoparticles entrapped cobalt oxide nanohairs/electrospun carbon nanofibers nanocomposite in apt architecture for high

performance supercapacitors. *Composites Part B: Engineering* **2019**, *178*, 107482, doi:https://doi.org/10.1016/j.compositesb.2019.107482.

96.   Wang, H.; Yang, X.; Wu, Q.; Zhang, Q.; Chen, H.; Jing, H.; Wang, J.; Mi, S.-B.; Rogach, A.L.; Niu, C. Encapsulating Silica/Antimony into Porous Electrospun Carbon Nanofibers with Robust Structure Stability for High-Efficiency Lithium Storage. *ACS Nano* **2018**, *12*, 3406-3416, doi:10.1021/acsnano.7b09092.

97.   Yan, J.; Dong, K.; Zhang, Y.; Wang, X.; Aboalhassan, A.A.; Yu, J.; Ding, B. Multifunctional flexible membranes from sponge-like porous carbon nanofibers with high conductivity. *Nature Communications* **2019**, *10*, 5584, doi:10.1038/s41467-019-13430-9.

98.   Yang, W.; Zhou, J.; Wang, S.; Zhang, W.; Wang, Z.; Lv, F.; Wang, K.; Sun, Q.; Guo, S. Freestanding film made by necklace-like N-doped hollow carbon with hierarchical pores for high-performance potassium-ion storage. *Energy & Environmental Science* **2019**, *12*, 1605-1612, doi:10.1039/C9EE00536F.

99.   Sun, M.-H.; Huang, S.-Z.; Chen, L.-H.; Li, Y.; Yang, X.-Y.; Yuan, Z.-Y.; Su, B.-L. Applications of hierarchically structured porous materials from energy storage and conversion, catalysis, photocatalysis, adsorption, separation, and sensing to biomedicine. *Chemical Society Reviews* **2016**, *45*, 3479-3563, doi:10.1039/C6CS00135A.

100.   Wu, H.B.; Lou, X.W. Metal-organic frameworks and their derived materials for electrochemical energy storage and conversion: Promises and challenges. *Science Advances* **2017**, *3*, eaap9252, doi:10.1126/sciadv.aap9252.

101.   Xie, X.-C.; Huang, K.-J.; Wu, X. Metal–organic framework derived hollow materials for electrochemical energy storage. *Journal of Materials Chemistry A* **2018**, *6*, 6754-6771, doi:10.1039/C8TA00612A.

102.   Li, Y.; Xu, Y.; Yang, W.; Shen, W.; Xue, H.; Pang, H. MOF-Derived Metal Oxide Composites for Advanced Electrochemical Energy Storage. *Small* **2018**, *14*, 1704435, doi:10.1002/smll.201704435.

103.   Arbulu, R.C.; Jiang, Y.-B.; Peterson, E.J.; Qin, Y. Metal–Organic Framework (MOF) Nanorods, Nanotubes, and Nanowires. *Angewandte Chemie International Edition* **2018**, *57*, 5813-5817, doi:10.1002/anie.201802694.

104.   Li, G.-C.; Liu, P.-F.; Liu, R.; Liu, M.; Tao, K.; Zhu, S.-R.; Wu, M.-K.; Yi, F.-Y.; Han, L. MOF-derived hierarchical double-shelled NiO/ZnO hollow spheres for high-performance supercapacitors. *Dalton Transactions* **2016**, *45*, 13311-13316, doi:10.1039/C6DT01791F.

105.   Yan, L.; Yuxia, X.; Wenping, Y.; Wanxin, S.; Huaiguo, X.; Huan, P. MOF-Derived Metal Oxide Composites for Advanced Electrochemical Energy Storage. *Small 0*, 1704435, doi:doi:10.1002/smll.201704435.

106.   Yu, C.; Wang, Y.; Cui, J.; Yu, D.; Zhang, X.; Shu, X.; Zhang, J.; Zhang, Y.; Vajtai, R.; Ajayan, P., et al. MOF-74 derived porous hybrid metal oxide hollow nanowires for high-performance electrochemical energy storage. *Journal of Materials Chemistry A* **2018**, *6*, 8396-8404, doi:10.1039/C8TA01426D.

107.   Na, K.; Choi, K.M.; Yaghi, O.M.; Somorjai, G.A. Metal Nanocrystals Embedded in Single Nanocrystals of MOFs Give Unusual Selectivity as Heterogeneous Catalysts. *Nano Letters* **2014**, *14*, 5979-5983, doi:10.1021/nl503007h.

108.   Xia, W.; Qu, C.; Liang, Z.; Zhao, B.; Dai, S.; Qiu, B.; Jiao, Y.; Zhang, Q.; Huang, X.; Guo, W., et al. High-Performance Energy Storage and Conversion Materials Derived from a Single Metal–Organic Framework/Graphene Aerogel Composite. *Nano Letters* **2017**, *17*, 2788-2795, doi:10.1021/acs.nanolett.6b05004.

109.   Muthurasu, A.; Chae, S.-H.; Kim, T.; Mukhiya, T.; Kim, H.Y. Template-Assisted Fabrication of ZnO/Co3O4 One-Dimensional Metal–Organic Framework Array Decorated with Amorphous Iron Oxide/Hydroxide Nanoparticles as an Efficient Electrocatalyst for the Oxygen Evolution Reaction. *Energy & Fuels* **2020**, *34*, 7716-7725, doi:10.1021/acs.energyfuels.0c01101.

110.   Tan, Y.; Meng, L.; Wang, Y.; Dong, W.; Kong, L.; Kang, L.; Ran, F. Negative electrode materials of molybdenum nitride/N-doped carbon nano-fiber via electrospinning method for high-performance supercapacitors. *Electrochimica Acta* **2018**, *277*, 41-49, doi:https://doi.org/10.1016/j.electacta.2018.04.214.

111.   Yang, Y.; Zhao, L.; Shen, K.; Liu, Y.; Zhao, X.; Wu, Y.; Wang, Y.; Ran, F. Ultra-small vanadium nitride quantum dots embedded in porous carbon as high performance electrode materials for capacitive energy storage. *Journal of Power Sources* **2016**, *333*, 61-71, doi:https://doi.org/10.1016/j.jpowsour.2016.09.151.

112.   Kim, C.; Yang, K. Electrochemical properties of carbon nanofiber web as an electrode for supercapacitor prepared by electrospinning. *Applied physics letters* **2003**, *83*, 1216-1218.

113.   He, Y.; Wang, L.; Jia, D. Coal/PAN interconnected carbon nanofibers with excellent energy storage performance and electrical conductivity. *Electrochimica Acta* **2016**, *194*, 239-245, doi:https://doi.org/10.1016/j.electacta.2016.01.191.

114.   Yu, Y.; Gu, L.; Zhu, C.; van Aken, P.A.; Maier, J. Tin Nanoparticles Encapsulated in Porous Multichannel Carbon Microtubes: Preparation by Single-Nozzle Electrospinning and Application as Anode Material for High-Performance Li-Based Batteries. *Journal of the American Chemical Society* **2009**, *131*, 15984-15985, doi:10.1021/ja906261c.

115.   Fu, B.; Zhou, X.; Wang, Y. Co3O4 carbon nanofiber mats as negative electrodes for sodium-ion batteries. *Materials Letters* **2016**, *170*, 21-24, doi:https://doi.org/10.1016/j.matlet.2016.01.132.

116.   Yao, S.; Guo, R.; Xie, F.; Wu, Z.; Gao, K.; Zhang, C.; Shen, X.; Li, T.; Qin, S. Electrospun three-dimensional cobalt decorated nitrogen doped carbon nanofibers network as freestanding electrode for lithium/sulfur batteries. *Electrochimica Acta* **2020**, *337*, 135765, doi:https://doi.org/10.1016/j.electacta.2020.135765.

117. Lu, F.; Wang, J.; Sun, X.; Chang, Z. 3D hierarchical carbon nanofibers/TiO2@MoS2 core-shell heterostructures by electrospinning, hydrothermal and in-situ growth for flexible electrode materials. *Materials & Design* **2020**, *189*, 108503, doi:https://doi.org/10.1016/j.matdes.2020.108503.

118. Heo, Y.-J.; Park, M.; Kang, W.-S.; Rhee, K.Y.; Park, S.-J. Preparation and characterization of carbon black/pitch-based carbon fiber paper composites for gas diffusion layers. *Composites Part B: Engineering* **2019**, *159*, 362-368.

119. Zhang, M.Y.; Niu, H.Q.; Qi, S.L.; Tian, G.F.; Wang, X.D.; Wu, D.Z. Structure evolutions involved in the carbonization of polyimide fibers with different chemical constitution. *Materials Today Communications* **2014**, *1*, 1-8, doi:https://doi.org/10.1016/j.mtcomm.2014.08.001.

120. Kuzmenko, V.; Wang, N.; Haque, M.; Naboka, O.; Flygare, M.; Svensson, K.; Gatenholm, P.; Liu, J.; Enoksson, P. Cellulose-derived carbon nanofibers/graphene composite electrodes for powerful compact supercapacitors. *RSC Advances* **2017**, *7*, 45968-45977, doi:10.1039/C7RA07533B.

121. Zhang, L.; Xia, G.; Guo, Z.; Sun, D.; Li, X.; Yu, X. In situ fabrication of three-dimensional nitrogen and boron co-doped porous carbon nanofibers for high performance lithium-ion batteries. *Journal of Power Sources* **2016**, *324*, 294-301, doi:https://doi.org/10.1016/j.jpowsour.2016.05.057.

122. Wei, J.; Geng, S.; Pitkänen, O.; Järvinen, T.; Kordas, K.; Oksman, K. Green Carbon Nanofiber Networks for Advanced Energy Storage. *ACS Applied Energy Materials* **2020**, *3*, 3530-3540, doi:10.1021/acsaem.0c00065.

123. Heo, Y.-J.; Zhang, Y.; Rhee, K.Y.; Park, S.-J. Synthesis of PAN/PVDF nanofiber composites-based carbon adsorbents for CO2 capture. *Composites Part B: Engineering* **2019**, *156*, 95-99, doi:https://doi.org/10.1016/j.compositesb.2018.08.057.

124. Yang, J.; Wang, Y.; Luo, J.; Chen, L. Highly nitrogen-doped graphitic carbon fibers from sustainable plant protein for supercapacitor. *Industrial Crops and Products* **2018**, *121*, 226-235, doi:https://doi.org/10.1016/j.indcrop.2018.05.013.

125. Lu, J.; Wan, H.; Ju, T.; Ying, Z.; Zhang, W.; Li, B.; Zhang, Y. Super flexible electrospun carbon/nickel nanofibrous film electrode for supercapacitors. *Journal of Alloys and Compounds* **2019**, *774*, 593-600, doi:https://doi.org/10.1016/j.jallcom.2018.09.383.

126. Tian, D.; Lu, X.; Nie, G.; Gao, M.; Wang, C. Direct growth of Ni–Mn–O nanosheets on flexible electrospun carbon nanofibers for high performance supercapacitor applications. *Inorganic Chemistry Frontiers* **2018**, *5*, 635-642, doi:10.1039/C7QI00696A.

127. Tian, S.; Jiang, Q.; Cai, T.; Wang, Y.; Wang, D.; Kong, D.; Ren, H.; Zhou, J.; Xing, W. Graphitized electrospun carbon fibers with superior cyclability as a free-standing anode of potassium-ion batteries. *Journal of Power Sources* **2020**, *474*, 228479, doi:https://doi.org/10.1016/j.jpowsour.2020.228479.

128. Kim, S.E.; Tiwari, A.P. Three dimensional polycaprolactone/cellulose scaffold containing calcium-based particles: a new platform for bone regeneration. *Carbohydrate Polymers* **2020**, *250*, 116880, doi:https://doi.org/10.1016/j.carbpol.2020.116880.

129. Tang, Z.; Zhang, G.; Zhang, H.; Wang, L.; Shi, H.; Wei, D.; Duan, H. MOF-derived N-doped carbon bubbles on carbon tube arrays for flexible high-rate supercapacitors. *Energy Storage Materials* **2018**, *10*, 75-84.

130. Cao, X.-M.; Sun, Z.-J.; Zhao, S.-Y.; Wang, B.; Han, Z.-B. MOF-derived sponge-like hierarchical porous carbon for flexible all-solid-state supercapacitors. *Materials Chemistry Frontiers* **2018**, *2*, 1692-1699.