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A Review of Electrospun Carbon Fibers as Electrode Materials for Energy Storage

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Abstract:

The applications of electrospun carbon fiber webs to the development of energy storages devices, including both supercapacitors and lithium ion batteries (LIB), are reviewed. Following a brief discussion of the fabrication process and characterization methods for ultrafine electrospun carbon fibers, recent advances in their performance as supercapacitors and LIBs anode materials are summarized. Optimization of the overall electrochemical properties of these materials through choice of thermal treatment conditions, incorporation of additional active components (such as carbon nanotubes, metal oxides, and catalysts), and generation of novel fibrous structures (such as core-shell, multi-channel or porous fibers) is highlighted. Further challenges related to improving the conductivity, surface area, and mechanical properties of the carbon nanofiber webs, as well as the scale-up ability of the fabrication technique, are discussed.

Keywords: electrospinning, carbon nanofiber, energy storage, supercapacitor, lithium-ion battery

1. Introduction

The development of energy storage devices is gaining extensive research interest due to growing world population, global climate change, concerns about exhaustion of fossil fuels, and the urgent need to meet the challenges for efficient storage of energy generated by some of the newer but intermittent sources such as solar and wind power. Supercapacitors[1-3] and lithium ion batteries (LIB)[4-7] represent the frontier of this research effort, and they have become increasingly important in our daily lives, powering numerous portable consumer electronic devices (e.g., cell phones, laptops, PDAs), hybrid electric vehicles, and even other heavy-duty industrial scale systems. The development of new materials that can provide efficient means for energy conversion and storage, as well as the advancement of our understanding of the electrochemical interfaces at the micro- or nanoscale, plays an essential role in the design of future generations of supercapacitor and LIB devices.

Supercapacitors (i.e., electrochemical capacitors) constitute a class of capacitors that contain an electrolyte solution in place of a dielectric layer. Recently there has been growing interest in the development of robust supercapacitor devices for energy storage and harvesting mainly because of their high capacitance, long cycle life, and superior power and energy density.[7-15] Depending upon the charge storage mechanism and the active materials used, supercapacitors are generally categorized as either electrochemical double layer capacitors (EDLC) or pseudocapacitors.[7] EDLCs store electrical energy using reversible physical adsorption of ions, without any chemical reactions, from an electrolyte solution onto two porous electrodes to form an electric double layer at an electrode-electrolyte interface (Figure 1). Supercapacitor devices can be composed using

the same material for the cathode and anode, in a symmetric device, or using different materials for each electrode, in an asymmetric device. Pseudocapacitors are fundamentally different from EDLCs in the way in which charge is stored, since they do not rely on the traditional charge separation mechanism that is typical of an electrostatic capacitor, but rather on a fast surface or near-surface Faradaic charge-transfer mechanism which gives them their "pseudo"-capacitive behavior. Highly porous carbon materials with high conductivity and electrochemical stability, such as activated, template and carbide-derived carbon, carbon fibers, fabrics, nanotubes, "onions", nanocages, nano-"horns", and graphene-based nanomaterials, have been researched extensively for EDLCs.[7,8,13-17] Well-known examples of pseudocapacitive materials include metal oxides[18,19] and conducting polymers,[7] which can rely on fast and reversible redox reactions that occur on the electrode surface to store energy.
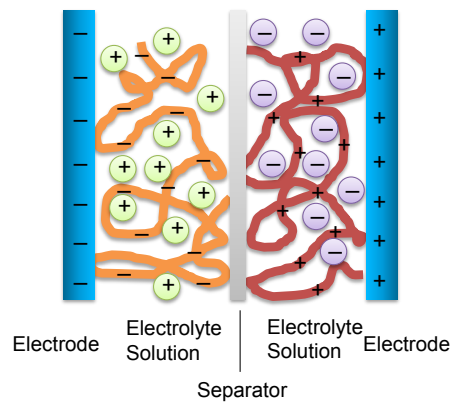
Figure 1. Schematic of an electrochemical double layer capacitor (EDLC). The thick orange and red lines represent conductive porous materials. The circles with the plus and minus signs represent the cations and anions in the electrolyte solution, respectively.

Lithium ion batteries were introduced in 1990 by Sony, following pioneering work by Whittingham, Scrosati and Armand.[20] LIBs have found significant applications in powering a great variety of electronic devices, and have recently been exploited in large scale applications such as in various types of electrical vehicles and in energy storage devices for utility grids. A typical commercial lithium-ion battery is composed of a graphite negative electrode (anode), a non-aqueous liquid electrolyte, and a positive electrode (cathode) formed from layered $LiCoO_2$ (Figure 2). Upon charging, lithium ions are extracted from the layered $LiCoO_2$ intercalation host, pass through the electrolyte solution, and intercalate between the graphite layers in the anode. Discharging is the reverse process, where the electrons transport through the external circuit. Extensively studied LIB anode materials include carbon,[21] silicon,[22-24] and tin,[25] among others, while the typical examples of cathode materials include $LiMn_2O_4$,[26,27] $LiFePO_4$,[28-30] and V_2O_5.[31] These research efforts aim to meet the increasingly challenging standards for the future applications of LIBs, such as improved energy density, power density, and cycle life.
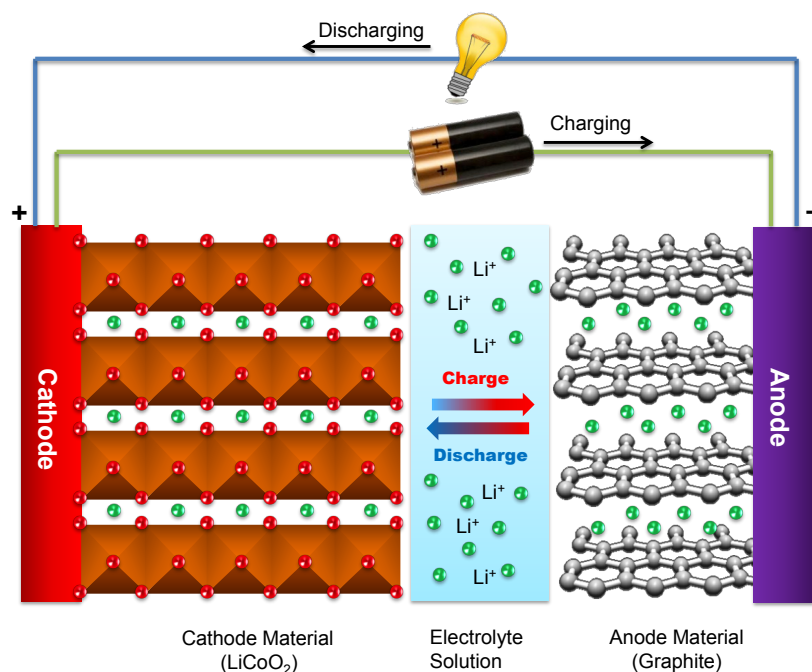
Figure 2. A typical configuration of a commercially available lithium ion battery illustrating the charging/discharging intercalation mechanism.

Electrospinning of an appropriate precursor solution to produce polymer fibers with submicron diameter, followed by thermal treatment to remove heteroatoms (i.e. to carbonize the polymer fibers), is a simple and low-cost approach to generate self-supported webs composed of continuous ultrafine carbon fibers.[32] The free-standing nature of the electrospun carbon fiber webs offers unique advantages for energy devices since it eliminates the need for using binders or substrates, thereby increasing the mass fraction of the active materials in a supercapacitor cell and improving the energy density. Moreover, processing conditions such as electrospinning parameters, composition of the precursor solution, and thermal treatment procedures can be used to control flexibly the morphology (e.g. fiber diameter, surface area, and porosity) as well as the electrical conductivity of the electrospun carbon fiber webs, which are two essential factors that

have significant effects on their electrochemical energy storage capabilities and rate performance.

In this review, following a brief discussion of the fabrication method for electrospun carbon fibers (i.e., electrospinning and thermal treatment) and their methods of characterization, we concentrate on the applications of electrospun carbon nanofiber webs to the development of energy storages devices, including both supercapacitors and lithium ion batteries.

2. Carbon Nanofibers Fabricated via Electrospinning and Thermal Treatment

2.1 Electrospinning of Polymer Solutions.

Electrospinning of polymer solutions gives rise to the generation of ultrafine fibers with diameters controlled to be in the micrometer to nanometer range. As shown in Figure 3, a conventional electrospinning set-up involves three major components: a high voltage power supply, a spinneret (e.g., a syringe or pipette tip), and a grounded collector (typically a flat metal plate or a rotating drum).[33] Briefly, the electrospinning technique is based on the application of an electric field to a drop of polymer solution on the tip of a spinneret. As the intensity of the electric field increases, the surface of this drop elongates to form a conical shape known as the Taylor cone (see Figure 4 (h)). When the applied electric field reaches a critical value, the repulsive electrical forces overcome the surface tension of the drop, and a charged jet of the solution is ejected from the tip of the cone and accelerates downfield. An electrohydrodynamic whipping instability of the jet occurs between the tip and the collector, which leads to further stretching of the liquid filament and the evaporation of the solvent to generate solidified continuous, micro- or

nanofibers on the grounded collector. Alternatively, jets can be generated from free liquid surfaces such as films, drops or bubbles, without the need for a spinneret; the subsequent acceleration, whipping and solidification to form fibers is similar to those in the conventional technique.[34] The often-cited advantages of electrospinning include ease of operation, efficiency, low cost, high yield, and high degree of reproducibility of the obtained materials. The versatility of electrospinning is reflected in the nature of electrospinnable materials as well as the different forms of fiber assemblies and architectures.
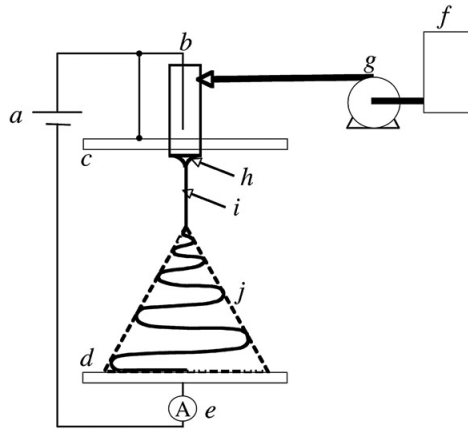
Figure 3. Schematic of the conventional electrospinning process. (a) high voltage power supply; (b) charging device; (c) high potential electrode (e.g. flat plate); (d) collector electrode (e.g. flat plate); (e) current measurement device; (f) fluid reservoir; (g) flow rate control; (h) cone; (i) thinning jet; (j) instability region. Reprinted with permission from reference 33. Copyright 2007 Elsevier.

2.2 Thermal Treatment of Polymer Fibers to Form Carbonaceous Fibers.

If a polymer with a high carbon yield (e.g., polyacrylonitrile (PAN) in most cases) is used to produce nanofibers from electrospinning, subsequent high temperature thermal

treatment can convert the polymer fibers to carbonaceous fibers. The formation of carbon fibers from precursor polymer fibers generally includes stabilization, carbonization, and sometimes activation (to modify morphology and surface chemistry) if high ion adsorption capacity or improved electrochemical properties are desired. Stabilization is necessary to prevent precursor fibers from fusing together during carbonization since this step converts thermoplastic precursor fibers to highly condensed thermosetting fibers by complicated chemical and physical reactions (e.g., dehydrogenation, cyclization and polymerization). It should be noted that the heating rate during stabilization is usually maintained at a relatively low value (e.g., 3 °C/min) to avoid the release of a large amount of heat that might cause loss of fiber orientation and melting of polymers. Carbonization is often carried out in an inert gas atmosphere (e.g. nitrogen or argon), which prevents oxidation, removes heteroatoms, and generates the pyrolysis products such as N_2, CO_2, H_2O, etc. This process is often accompanied by a morphological change from smooth polymer fiber to wrinkled carbonaceous fibers with a decrease in fiber diameter and an increase in surface area.

2.3 Characterization Methods of Electrospun Carbon Nanofibers

The morphology of electrospun carbon fibers, such as fiber diameter and surface topology, is usually characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specific surface area and average pore size can be estimated from nitrogen adsorption isotherms, based on the Brunauer-Emmett-Teller (BET) method .[16,35] Mesopore and micropore size distributions can be measured using the Barrett-Joiner-Halenda (BJH)[16] and Horvath-Kawazoe (HK) approaches,[35] respectively. The degree of carbonization and important microstructural information can

be estimated from Raman spectroscopy, electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Raman analysis provides the relative intensity of the D and G bands (R_I), an indicator of the relative proportion of disordered to graphitic carbon.[36] EELS can be used to quantify the ratio between the π orbitals and σ orbitals, which is 1/3 and 0/4 for purely sp^2 and sp^3 bonded carbons, respectively. If a reference sample that contains purely sp^2 carbon is available (such as a standard graphite),[15] the π/σ ratio can be converted to the sp^2/sp^3 ratio.[15,37] XPS C 1s spectra provide direct measurements of the sp^2/sp^3 ratio based on the deconvolution of the high-resolution C 1s peak into the sp^2-bonded and sp^3-bonded components.[38,39] The crystallite size (L_c) and interlayer spacing (d_{002}) can be estimated from XRD using the Scherrer and Bragg equations, respectively.[40] The electrical conductivity of electrospun CNF mats is usually measured using a four-probe or a two-probe method. The four-probe method works well for webs composed densely-packed fibers when the electrical contacts are good between the fibers and the probes. This method avoids the contact resistance and gives direct measurement of sheet resistance. However, the four-probe method may give inconsistent results if the electrospun webs are highly porous, leading to poor contacts between fibers and the probes. The two-probe method is suitable for highly porous samples since the electrical contacts between the webs and the probes are made through the use of a conductive foil (such as a copper tape). It should be noted that in the two-probe method a correction should be made for the contact resistance, which can be obtained by varying the distance between the two probes, plotting the resistance versus the probe spacing and extrapolating the best linear fit to zero probe spacing.[41] The electronic structures (i.e., valence band structures or density of electronic states) can be

investigated using ultraviolet photoelectron spectroscopy (UPS). It is noteworthy that information on the density of states for semi-metal carbonaceous materials can also be inferred from their electrical conductivity.[42,43]

3. Electrospun carbon fibers for supercapacitor applications

As mentioned earlier, various forms of porous carbons such as activated fibers, templated carbons, and carbon nanotubes have been investigated for supercapacitor applications. Electrospun carbon fibers webs, which can be fabricated with varying fiber diameter, porosity and surface chemistry, enjoy unique advantages for the improvement of capacitor performance. Kim *et al.* first reported the application of electrospun carbon fibers to the development of supercapacitor devices.[44] Following this report, several other groups developed various modifications and new fabrication methods to improve the electrochemical properties of electrospun carbon fibers for supercapacitor applications; these studies are listed in Table 1 with a summary of (1) the composition of the precursor solution, (2) thermal treatment conditions, (3) fiber diameter, (4) surface area, and (5) electrocapacitive performance.

Table 1. Electrospun CNF-based supercapacitor electrode materials.

Precursor solution	Thermal treatment conditions	Fiber diameter (nm)	Surface area (m^2/g)	Electrocapactive performance	Ref.
10 wt% PAN in DMF	Stabilized at 280 °C, carbonized and activated at 700 – 800 °C in N_2 and steam	200 – 400	1230	173 F/g at 10 mA/g in 30 wt% KOH	44
20 wt% PBI in DMAc	Carbonized and activated at 750 – 850 °C for 0.5 h and activated in N_2 and steam	100 – 500	1220	178 F/g at 5 mA/g in 30 wt% KOH	45,46
10 wt% PAN in DMF	Stabilized at 280 °C, carbonized and activated at 800 °C in N_2 and steam	200 – 350	1160	134 F/g at 1 mA/cm^2 In 6 M KOH	47
PAA in THF and MeOH	Imidized at 350 °C, carbonized at 1000 °C, and activated at 800 in N_2 and	2000 – 3000	940 – 2100	175 F/g at 1000 mA/g in 30 wt% KOH	48

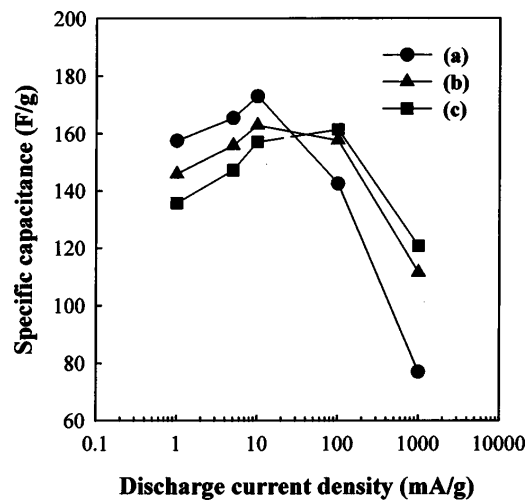|	steam				
20 wt% PBI in DMAc	Carbonized and activated at 700 – 850 °C for 0.5 h in N_2 and steam	230	500 – 1220	202 F/g in 1 M H_2SO_4 at 1 mA/cm²	49
PAN and Ru-acac in DMF	Stabilized at 280 °C, carbonized and activated at 800 °C in N_2 and steam	200 – 900	428 – 531	391 F/g with 7.31 wt% Ru content in 6 M KOH at 1 mA/cm²	50
10 wt% PAN and $ZnCl_2$ in DMF	Stabilized at 280 °C, carbonized at 800 °C	200 – 350	310 – 550	140 F/g in KOH	51
10 wt% PAN and 3 wt% MWCNT in DMF	Stabilized at 280 °C, carbonized and activated at 800 °C, coated by PPy	230	742	333 F/g in 6 M KOH at 1 mA/cm²	52
10 wt% PAN and 10 wt% V_2O_5 in DMF	Stabilized at 250 °C, carbonized and activated with KOH at 800 °C,	-	2800	128 F/g in 1 M $(C_2H_5)_4NBF_4$/PC at 1 A/g	35
PAN and CA in DMF	Stabilized at 280 °C, carbonized and activated at 800 °C	250 – 700	1160	245 F/g in 6 M KOH at 1 mA/cm²	53
7.2 wt% PAN and 0.8 wt% MWCNT in DMF	Stabilized at 240 °C, carbonized at 700 °C, and activated with H_2O_2 vapor at 600 °C	~ 500	810	310 F/g in 1 M H_2SO_4 at 100 mA/g	54
PAN and Ni(OAc) in DMF	Stabilized at 280 °C, carbonized at 1000 °C	150 – 210	-	164 F/g in 6 M KOH at 2 mV/s and at 250 mA/g	55
PAN and PVP in DMF	Stabilized and carbonized from 300 – 970 °C, activated by CO_2 at 850 °C	-	531	220 F/g in 1 M H_2SO_4	56
PAN and TEOS in DMF	Stabilized at 280 °C, carbonized at 800 – 1000 °C	150	980 – 1200	160 F/g in 6 M KOH at 1 mA/cm²	57
PAN and $AgNO_3$ in DMF	Stabilized at 280 °C, carbonized and activated at 800 °C in N_2 and steam	350	1096	150 F/g in 6 M KOH at 1 mA/cm²	58
PAN in DMF + pitch in THF	Stabilized and carbonized at 1000 °C	150	966	130 F/g in 6 M KOH at 1 mA/cm²	59
PAN and Ag nanoparticles in DMF	Stabilized at 250 °C and carbonized at 1000 °C in N_2	200 – 500	-		60

Note (abbreviations in the table): PAN: polyacrylonitrile. PBI: polybenzimidazole. PAA: poly(acmi acid). CA: cellulose acetate. OAc: acetate. PVP: polyvinylpyrrolidone. TEOS: tetraethoxy orthosilicate. MWCNT: multi-walled carbon nanotube. DMF: N,N-dimethylformamide. DMAc: dimethylacetamide. MeOH: methanol. THF: tetrahydrofurane.

Improvements in the electrochemical capacitance of electrospun carbon nanofibers have been achieved generally by three types of strategies: (1) manipulation of fiber morphology and degree of graphitization by control of heat treatment conditions, use of catalysts during carbonization and/or activation, selection and combination of different polymer precursors such as PAN, polybenzimidazol (PBI), poly(amic acid) (PAA), pitch, polyvinylpyrrolidone (PVP) and cellulose acetate (CA); (2) inclusion of pseudocapacitive contribution into the carbon nanofibers through incorporation of redox-active components such as metal oxides and conducting polymers; and (3) improvement

of electrical conductivity by encapsulation of highly conductive components such as carbon nanotubes and metallic nanoparticles.

The effects of steam activation temperature on the electrocapacitive performance of PAN-based electrospun carbon fiber webs are summarized in Figure 4, which shows the specific capacity as a function of discharge current density for carbon fiber webs activated at 700, 750 and 800 °C in steam. [44] The maximum specific capacitance obtained was 175 F/g at 10 mA/g for the carbon fiber web activated at 700 °C (Figure 4a); however the capacitance dropped quickly to 75 F/g, with an increase in current density to 1000 mA/g. Interestingly, the carbon fiber webs synthesized at 800 °C exhibited the highest capacitance of 120 F/g at the higher current density of 1000 mA/g (Figure 4c). This was attributed to the high fraction of mesopore volume obtained at 800 °C, since the ions solvated by water molecules in the mesopores would respond more quickly than those in the micropores at a higher current density. Zinc chloride, which acts as a catalyst for carbonization of PAN, was used to control fiber diameter and surface area of PAN-based electrospun carbon fibers.[51] As shown in Figure 5, with increasing zinc chloride content from 1 to 3 to 5 wt%, the average diameters of the fibers decreased from 350 to 250 to 200 nm, respectively. After carbonization, the sample with 5 wt% zinc chloride exhibited the highest capacitance, probably because it had the largest surface area, resulting from the catalytic activity of zinc chloride. Electrospinning of a solution of nickel acetate and PAN in DMF, followed by stabilization and carbonization, generated nickel-embedded carbon fibers.[55] The specific capacitance of the carbon fiber electrode without the Ni loading was only 50 F/g, while the value for 22.4 wt% Ni/carbon electrode increased to 164 F/g. This increase was ascribed to the electrochemical catalysis effect of

nickel. Microporous structures on the electrospun carbon fibers can also be created by incorporating tetraethoxy orthosilicate (TEOS) into PAN solution to improve the electrochemical capacitance.[57] Using vanadium catalyst, pore size control in electrospun carbon fibers was achieved.[35] In addition, electrospinning of bicomponent polymer solutions such as PAN/CA[53], PAN/PVP[56], and PAN/pitch[59] have been investigated to modulate the resulting carbon fiber structures and their capacitive behavior.

Figure 4. Specific capacitance as a function of discharge current density for PAN-based electrospun carbon fiber webs treated at various activation temperatures in steam: (a) 700, (b) 750, and (c) 800 °C. Reprinted with permission from reference 44. Copyright 2003 American Institute of Physics.
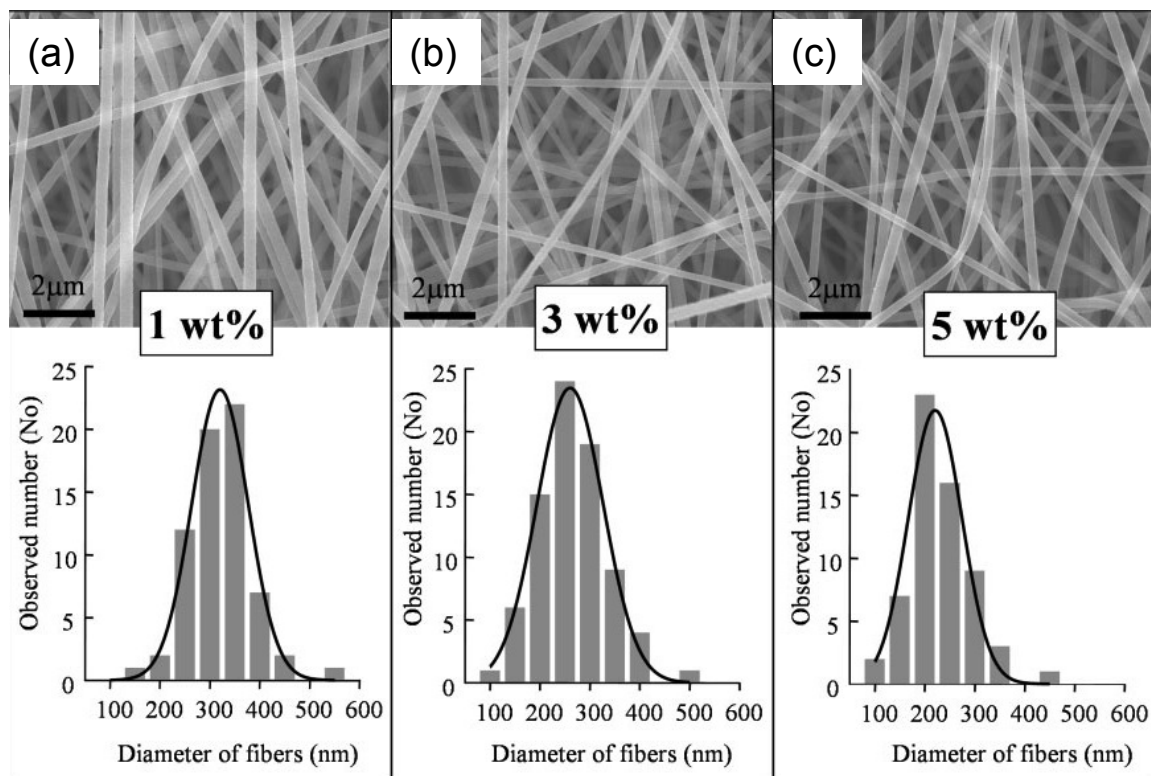
Figure 5. Field-emission scanning electron microscopy (FE-SEM) images of the electrospun organic fibers from PAN solutions containing different weight percents of zinc chloride, c) 1, d) 3, and e) 5 wt%, and their corresponding diameter distributions. Reprinted with permission from reference 51. Copyright 2007 WILEY-VCH.

Incorporation of redox-active species into electrospun carbon fibers can improve significantly their electrochemical capacitance due to the simultaneous use of both charge storage mechanisms (i.e., electrical double layer and redox reactions). Ruthenium-embedded carbon fibers were prepared by the processes of stabilization, carbonization, and activation after electrospinning a composite solution of ruthenium (III) acetylacetonate and PAN in DMF.[50] The specific capacitances were enhanced greatly after incorporation of Ru nanoparticles into the carbon fibers. Figure 6 shows that the total capacitance (EDLC and pseudocapacitance combined) of the Ru-loaded carbon

fibers increased with Ru content. The capacitance of electrospun carbon fibers without Ru was 140 F/g whereas the value for the electrode with 7.31 wt% Ru was increased to 391 F/g. This was attributed to the synergistic effects of enhanced electric double-layer capacitance as a result of the expansion of the average pore diameter as well as the added pseudocapacitance by the well-dispersed Ru nanoparticles.
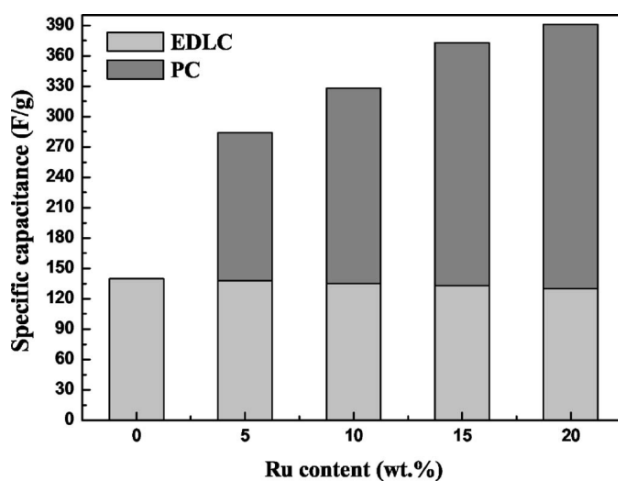
Figure 6. Specific capacitance of ruthenium-loaded electrospun carbon fiber electrodes at different Ru content. EDLC represents the contribution from the electrical double layer capacitance, while PC represents the contribution from the pseudocapacitance of Ru. Reprinted with permission from reference 50. Copyright 2007 The Electrochemical Society.

Improving the electrical conductivity of carbon fibers by loading highly conductive components is another approach to enhancing their electrochemical performance. Electrospinning is a unique method that can produce CNT-embedded fibers as a type of non-woven web.[52,54] The electrochemical performance of the CNT-loaded fiber webs depends on how well the CNTs are distributed with the fiber webs. Three wt% MWCNT were dispersed in a 10 wt % PAN/DMF solution using a homogenizer, and the resultant

CNT-embedded carbon fiber webs obtained after electrospinning and carbonization exhibited an increased EDLC capacitance of 180 F/g in 6 M KOH.[52] This was explained by the observation that the addition of MWCNTs increased both the BET surface area and electrical conductivity of the electrospun carbon fibers. Moreover, coating of polypyrole (PPy) on the MWCNT-loaded fibers resulted in a further increase in capacitance due to the pseudocapacitive contribution from the electrochemically active polymer PPy. Silver nanoparticle-containing carbon fibers were prepared through electrospinning of a mixture of silver powders and PAN in DMF, followed by stabilization in air at 250 °C for 2 h and carbonization in N_2 at 1000 °C for 2 h.[60] A ten-fold decrease in resistance was observed when 1 wt % silver nanoparticles were incorporated into the carbon fibers, compared to the case without silver loading. Only slight improvement in conductivity was found when the silver concentration was further increased to 5 wt%. For the 1 wt% silver concentration, the resistance was 4.5×10^{-2} $\Omega \cdot cm$, and for 3 wt% and 5 wt%, it was 4.0×10^{-2} and 3.5×10^{-2} $\Omega \cdot cm$, respectively. However, when the silver content increased from 0 to 1 to 3 to 5 wt%, the specific capacitance of the carbon fiber webs was enhanced significantly from 190 to 224 to 234 to 248 F/g.

4. Electrospun carbon nanofibers as anode materials for lithium-ion batteries

Rechargeable lithium-ion batteries now dominate the portable electronic market. Various types of carbonaceous materials including carbon particles, carbon nanotubes and carbon fibers have been investigated for LIB applications. Compared to natural graphite, which has a relatively low theoretical Li^+ storage capacity of 372 mAh/g, PAN-derived electrospun carbon fibers thermally treated at 1000 °C have been found to exhibit

a slightly higher reversible discharge capacity of 450 mAh/g.[61] However, higher

temperature treatment (2800 °C) led to a remarkable decrease in the LIB reversible

capacity. To improve LIB performance, it is often necessary to incorporate into the

carbon matrix another component that has a high Li^+ storage capacity such as silicon (Si)

or tin (Sn). Table 2 provides a summary of reports that describe electrospun carbon fiber-

based materials for LIB anode applications, with emphasis on: (1) the composition of the

precursor solution; (2) thermal treatment conditions; (3) functionalities/active

components; and (4) optimal reversible capacity achieved in each case, often using

different testing conditions or material compositions.

Table 2. Electrospun carbon fiber-based anode materials for lithium-ion batteries.

Precursor solution	Thermal treatment conditions	Functionalities/active components	Optimal reversible capacity (mAh/g)	Ref.
10 wt% PAN in DMF	Stabilized at 280 °C, carbonized at 700 – 2800 C in N_2	Non-graphtizable carbon formed at different pyrolysis temperatures	450	61
PAN and $Co(OAc)_2$ in DMF	Stabilized at 230 °C, carbonized at 600 °C	40 wt% Co loaded	750	62
PAN and Fe-acac in DMF	Stabilized at 240 °C, carbonized at 700 °C	Fe_3O_4 loaded	1007	63
PAN and $Mn(OAc)_2$ in DMF	Stabilized at 240 °C, carbonized at 700 °C	MnO and Mn_3O_4 loaded	800	64
PAN, poly-L-lactic acid and Si in DMF	Stabilized at 240 °C, carbonized at 700 °C	Si nanoparticle loaded	1100	65
PAN in DMF and TBT in mineral oil	Dissolved out mineral oil in n-octane, carbonized at 1000 °C	Sn@carbon nanoparticles	737	66
PAN, PMMA and tin octoate in DMF	Stabilized at 250 °C, carbonized at 1000 °C	Multi-channels by removal of PMMA during carbonization, tin nanoparticle loaded	648	67
PAN and $ZnCl_2$ in DMF	Stabilized at 280 °C, carbonized at 700 °C, Zn washed out by HCl	$ZnCl_2$ mixed carbon fibers	400	68
PAN and Si in DMF	Stabilized at 280 °C, carbonized at 700 °C	Si filled carbon (Si/C)	855	69
PVA and Si in water and Na alkyl-benzenesulfonate	Heat treated at 500 °C	Si nanoparticle loaded	892	70
PAN and Si in DMF	Stabilized at 280 °C, carbonized at 700 °C	Si nanoparticle loaded	1281	71
PAN and fumed SiO_2 in DMF	Stabilized at 280 °C, carbonized at 1000 °C, SiO_2 washed out by HF	Porous carbon fibers created by removal of SiO_2	593	72
PAN and $Ni(OAc)_2$ in DMF	Stabilized at 280 °C, carbonized at 600 °C	Ni nanoparticles dispersed in carbon fibers	795	73
PAN and $Mn(OAc)_2$ in	Stabilized at 280 °C, carbonized at 700 °C	MnO_x loaded	785	74

DMF				
PAN and poly-L-lactic acid in DMF	Stabilized at 280 °C, carbonized at 800 °C	Porous carbon fibers from bicomponent precursor solution	435	[75]
PVA and SnCl₂ in H₂O	carbonized at 500 °C	Sn/C composite fibers	382	[76]
PVA and SnCl₂ in H₂O	carbonized at 550 °C	Sn and SnO_x loaded	510	[77]
PAN and $Cu(OAc)_2$ in DMF	Stabilized at 280 °C, carbonized at 600 °C	FCC-Cu loaded	617	[78]
PAN and Si in DMF	carbonized at 800 – 1200 °C	Si nanoparticles loaded	500	[79]
PAN and $LiFePO_4$ in DMF	Stabilized at 280 °C, carbonized at 700 °C	$LiFePO_4$/C composite fibers	160	[80]
PAN, PMMA and Si in DMF	Stabilized at 280 °C, carbonized at 1000 °C	Si@C core-shell fibers	1384	[81]

Note (abbreviations in the table): PAN: polyacrylonitrile. PBI: polybenzimidazole. PAA: poly(acmi acid). PMMA:poly(methyl methacrylate). CA: cellulose acetate. OAc: acetate. TEOS: tetraethoxy orthosilicate. acac: acetylacetonate. TBT: tributyltin. PVA: poly(vinyl alcohol). FCC: face-centered cubic. DMF: N,N-dimethylformamide.

Si has been considered an excellent candidate for next-generation LIB anode materials since it has the highest known theoretical capacity of 4200 mAh/g, significantly greater than the values for graphite and metal oxides.[23,82] However, Si can experience large volume changes due to severe pulverization upon lithium insertion and extraction, which leads to reduced capacity and cycling stability.[83] Dispersion of Si nanoparticles in a carbon matrix, which acts as both a structural buffer and an electroactive material, proves an effective strategy to improve the LIB performance of Si. Electrospinning of PAN and Si in DMF, followed by thermal treatment, generated carbon fibers with Si nanoparticles distributed both inside and on the surfaces of the fibers. These Si/C fibers were found to show good capacitive retention when tested as LIB anode materials.[64,71] Porous carbon fibers that contained Si nanoparticles were prepared through carbonization of composite fibers of PAN, PLLA and Si, which exhibited large reversible capacity and relatively good cycling performance with a high current density of 200 mAh/g.[65] Recently, Hwang et al.[81] reported an electrospinning process to produce core-shell fiber electrodes using a coaxial nozzle (Figure 7). Si nanoparticles in the core were wrapped by the carbon shell. Various issues of Si-based anode operations, such as pulverization,

vulnerable contacts between Si and carbon conductor, and an unstable solid-electrolyte interface, were simultaneously addressed by the unique core-shell structure. Therefore the Si/C core-shell fibers showed a gravimetric capacity as high as 1384 mAh/g, a 5 min discharging rate capability with a capacity of 721 mAh/g, and a cycle life of 300 cycles with almost no capacity loss.
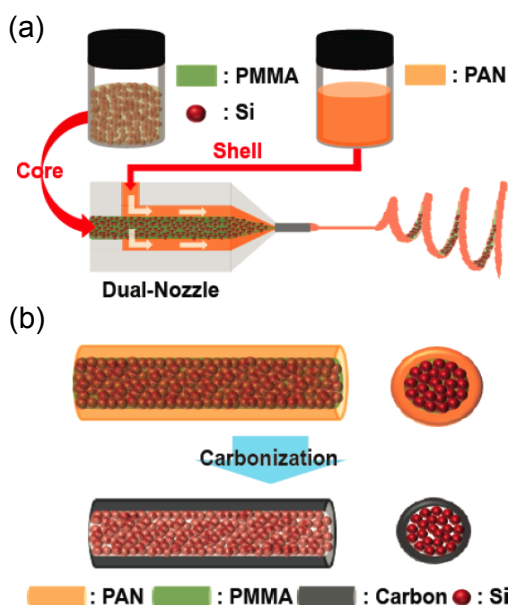
Figure 7. Schematic illustration of the electrospinning and carbonization steps to produce core-shell Si/C fibers. (a) The electrospinning process using a coaxial nozzle. The PMMA solution containing Si nanoparticles and the PAN solution were injected into the core and shell channels of the nozzle, respectively. (b) After electrospinning, stabilization, and carbonization steps were employed to complete the core−shell 1D fibers consisting of Si nanoparticlse and carbon, respectively. Reprinted with permission from reference 81. Copyright 2012 American Chemical Society.

Metallic tin (Sn) has also attracted tremendous interest as an anode material for LIBs due to its relatively high theoretical capacity of about 990 mAh/g. Practical applications of Sn

to LIBs is hampered by the poor cycling stability that results from the substantial volume changes that occur during charging and discharging. Electrospun carbon fibers with dispersed tin nanoparticles have been shown to improve the cycling stability of tin anodes considerably. "Sn@C" nanoparticles (comprising a Sn core wrapped by a thin, 10nm carbon layer) encapsulated in bamboo-like hollow carbon fibers were synthesized by carbonization of coaxially electrospun fibers.[66] Specifically, as shown in Figure 8a, the Sn@C composite fibers were prepared by the electrospinning of PAN fibers containing tributyltin (TBT) dissolved into a mineral oil, followed by extraction of the mineral oil, most of which was located in the cores of the fibers, by n-octane, and finally by heating the fibers at 1000 °C in an Ar/H$_2$ atmosphere to carbonize the outer PAN shell and to decompose the TBT core to metallic Sn. The Sn/C composite electrode was compared to a commercial Sn nanopowder electrode in terms of the cycling performance (Figure 8b). The Sn/C composite electrode exhibited improved cycling performance and a high reversible specific capacity of over 800 mAh/g for the first 10 cycles, while maintaining a reversible capacity of about 737 mAh/g after 200 cycles. In contrast, the Sn nanopowder electrode had a discharge capacity that dropped rapidly after the first 40 cycles. Moreover, the Sn/C composite electrode exhibited excellent rate performance (Figure 8c): it delivered a rate capacity of about 650 mAh/g when first cycled at 1 C (where 1 C rate represents a one-hour complete charge or discharge),[84] 550 mAh/g at 3 C, 480 mAh/g at 5 C, and finally back to 610 mAh/g at 1 C again. Another type of Sn/C composite electrode, porous multichannel carbon microtubes (SPMCTs) with Sn nanoparticles encapsulated, was prepared via the single-nozzle electrospinning of PMMA/PAN/tin octoate precursor solution and subsequent carbonization to remove PMMA and reduce tin

oxide to tin nanoparticles (Figure 9).[67] The SPMCT electrode also showed significantly improved cycling performance compared to the electrode made of Sn nanopowder alone. Electrospun carbon fibers with Sn nanoparticles incorporated were also synthesized using PVA as the precursor polymer.[76,77]
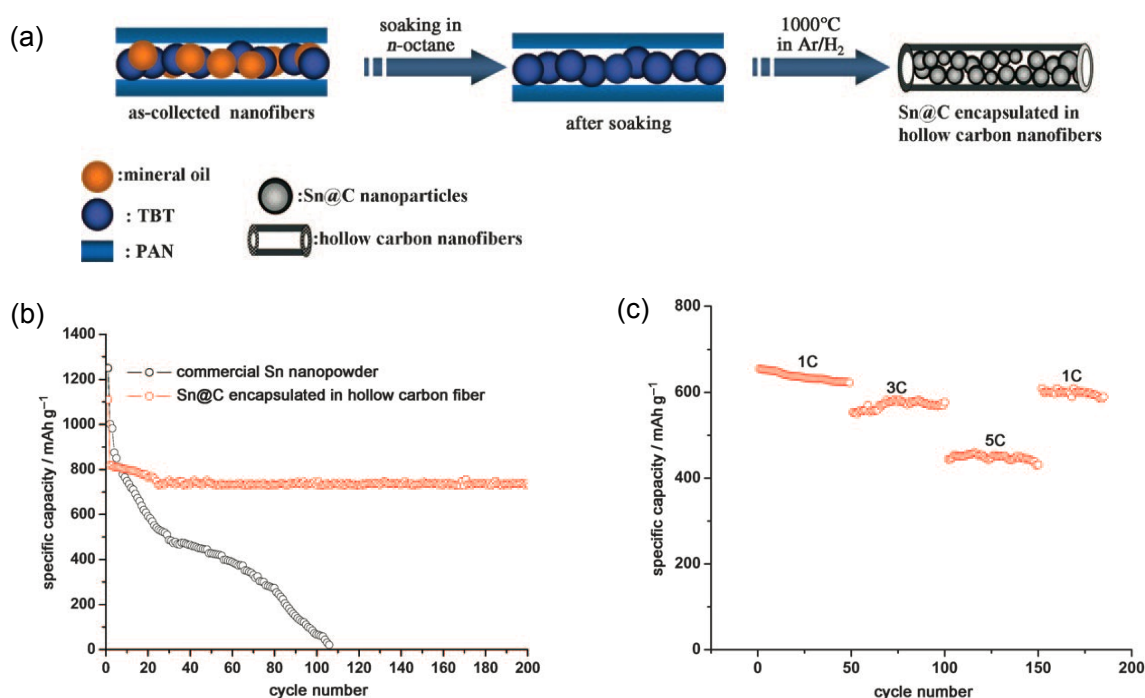
Figure 8. (a) Schematic illustration of preparation of Sn@carbon nanoparticles encapsulated in hollow carbon fibers. (b) Capacity – cycle number curves of a Sn/C composite electrode and a commercial Sn nanopowder (diameter: 100 nm) electrode at a cycling rate of 0.5 C. (c) Discharge capacity of a Sn/C composite electrode as a function of discharge rate (1 – 5 C). Reprinted with permission from reference 66 . Copyright 2009 WILEY-VCH.
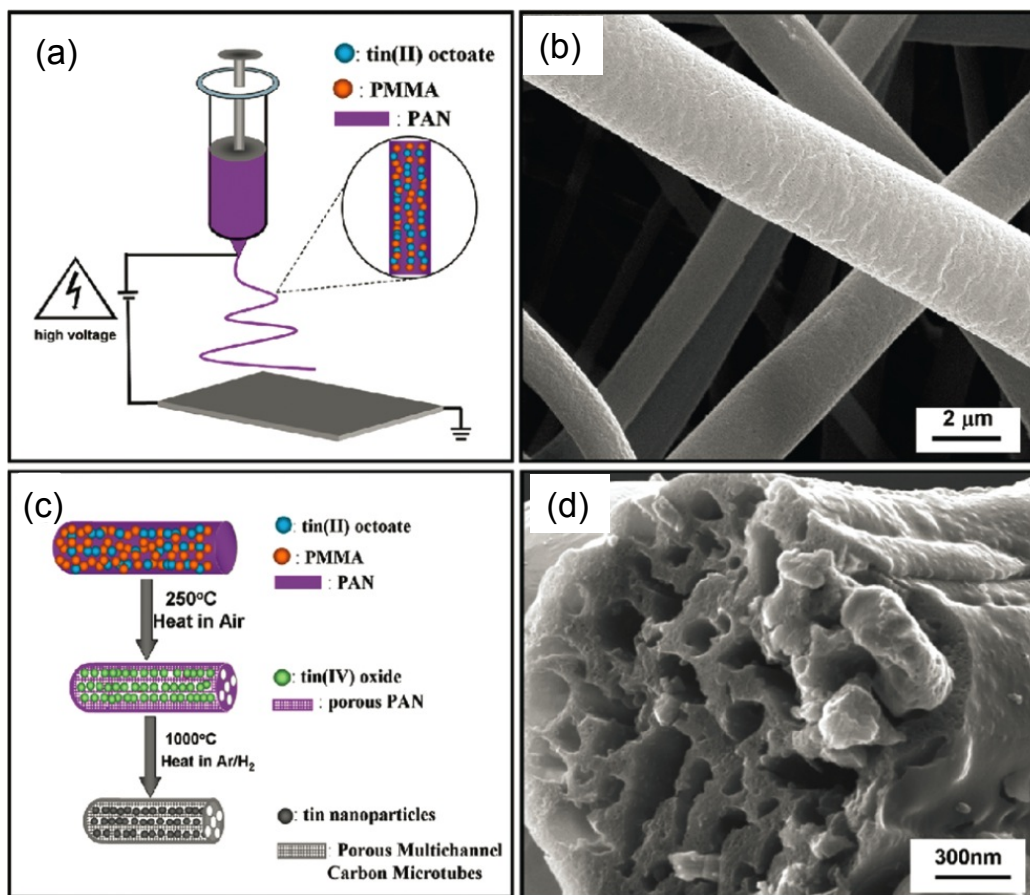
Figure 9. (a) Schematic illustration of co-electrospinning of a PMMA-PAN-tin octoate mixture in DMF using a single-needle nozzle. The inset (right) shows a magnified cartoon of the liquid filament. In the inset, the PMMA/DMF droplets are illustrated in orange, while the PAN/DMF liquid and tin octoate are illustrated in purple and dark-blue, respectively. (b) Scanning electron microscopy (SEM) images of the as-collected core-shell fibers obtained via the single-nozzle electrospinning technique. (c) Proposed synthetic scheme for Sn nanoparticles encapsulated in porous multichannel carbon microtubes (SPMCTs). (d) High-magnification cross-sectional image of carbonized PMMA-PAN-tin octoate fibers that reveals the tubular structure of the SPMCTs. Reprinted with permission from reference 67. Copyright 2009 American Chemical Society.

To improve LIB performance, other electrochemically active metallic particles such as Co,[62] Fe,[63], Mn,[64,74] Ni[73], and Cu[78] have also been incorporated into PAN-derived electrospun carbon fibers. Co/C composite fibers with diameters from 100 to 300 nm were found to exhibit a high reversible capacity of over 750 mAh/g and good rate capability of 678 mAh/g at 1 C.[62] These improvements, compared to the LIB performance of pure carbon fibers, were ascribed to the incorporation of cobalt that led to an increase in the interfacial surface area between carbon and liquid electrolyte as well as an enhanced electronic conductivity. Fe_3O_4 has a higher lithium ion storage capacity (924 mAh/g) than does natural graphite. Electrospun Fe_3O_4/C fibers, annealed at a low temperature of 700 °C to generate disordered carbon and nanocrystalline Fe_3O_4 , have been reported to show a very high capacity of 1007 mAh/g at the 80th cycle and good rate capability. [63] Mn or Ni or Cu -loaded porous carbon fibers were prepared through electrospinning of PAN/Mn(OAc)$_2$ or Ni(OAc)$_2$ or Cu(OAc)$_2$ in DMF and were found to exhibit improved electronic conductivity and enhanced lithium storage.[64,73,74,78]

5. Opportunities and challenges

Electrospun carbon fibers have been synthesized by various techniques and enjoy the advantages of controllable fiber diameter, surface area, surface chemistry and degree of graphitization. Therefore these materials represent a promising platform technology for the development of energy storage devices, in particular for supercapacitors and lithium ion batteries. Conventional approaches for the preparation of carbon fibers include the substrate, spraying, vapor growth and plasmon-enhanced chemical vapor deposition methods. Compared to these techniques, electrospinning of precursor solutions

followed by thermal treatment is a versatile and cost-effective fabrication method to produce 1-dimensional substrate-free mesostructured or nanostructured carbon-based materials, with the additional possibility to induce ordered internal morphologies such as core-shell, hollow or porous fibers, or multichannelled microtube configurations. The breadth of structural variability is a result of the considerable flexibility of this technique (1) to accommodate variations in composition of the precursor solutions, such as incorporation of carbon nanotubes, surfactants, catalysts, metal oxides, and multi-component polymer mixtures, (2) to respond to differences in electrospinning parameters such as voltage, flow rate, single or dual nozzles, and collector types, and (3) to accommodate variations in thermal treatment conditions to modulate carbonization degree and therefore the microstructural parameters such as graphite crystal size, interlayer spacing, and the sp^2/sp^3 ratio. Moreover, the energy storage capabilities of electrospun carbon nanofiber-based electrodes are competitive with those of commercial supercapacitor and LIB devices. Caution should be exercised, however, when comparing the electrochemical performance of carbon nanofiber electrodes with those of commercial devices since many of the literature sources report the energy storage values relative to the mass of the active material, not to the total mass of the device. Commercial supercapacitors can attain a capacitance of ~4000 F with a cell mass of ~0.5 kg (i.e., ~8 F/g cell),[85] Generally the weight of the active material accounts for approximately 10% of the total cell mass for supercapacitor devices, and thus the gravimetric capacitance of commercial supercapacitors with respect to the mass of the active material is ~ 100 F/g. Commercial LIBs usually exhibit a reversible capacity of 1000 mAh with a battery mass of ~0.5 kg,[86] giving a gravimetric capacity of 10 mAh/g with respective to the mass of the

anode material. As shown in Tables 1 and 2, the supercapacitor capacitances (F/g) and LIB capacity (mAh/g) of various electrospun carbon fiber-based electrode materials already exceed the corresponding values for commercial devices. In addition to carbon nanofibers, other forms of nanocarbons, in particular carbon nanotubes and graphenes, have also been investigated extensively as next-generation energy storage materials. In CNT or graphene-based energy storage devices, substrates or binders are usually required, which may reduce the energy densities and power densities of such devices due to the necessary incorporation of additional inactive materials. However, CNTs and graphene have remarkably higher surface areas and electrical conductivities than do electrospun carbon fibers. These properties provide for enhanced energy storage capacity as well as an excellent rate capability, due to simultaneously facilitated electron transport, ion diffusion and redox reaction rates. Therefore, development of electrospun carbon fibers with improved conductivity and high surface area, as well as controlled pore size/distribution and new chemical functionalities is essential to meet the current challenges for energy-related applications such as improving power density for supercapacitor devices as well as increasing lithium ion storage capacity and rate performance for LIB applications.

High conductivity is of great significance for the development of both supercapacitor devices and LIBs. However, conductivities of electrospun carbon nanofibers are usually significantly lower than those of graphenes and carbon nanotubes because the carbon precursor used in electrospinning, PAN in most cases, cannot achieve a high degree of graphitization during carbonization. PAN-derived electrospun carbon nanofibers are not completely graphitized even when carbonized at a very high

temperature of 2800 °C, as evidenced by an interlayer spacing of 0.341 nm and a low electrical conductivity of 20 S/cm.[61] In order to improve conductivities, carbon nanotubes and metallic nanoparticles have been incorporated into PAN-based carbon fibers. A high content of metal nanoparticles or CNTs leads to poor electrospinnability of the precursor solution, however, and only minor improvements in conductivity have been achieved through the addition of conductive components into the precursor mixtures. For example, incorporation of 0.8 wt% MWCNTs gave rise to a small increase in electrical conductivity from 0.86 to 5.32 S/cm for electrospun carbon fiber webs treated at 700 °C.[54], Chemical modification of electrospun carbon fibers after thermal treatment to improve conductivities and electrochemical capacitances for supercapacitor applications, on the other hand, has not received as much attention. Opportunities exist to exploit post-carbonization chemical modification techniques to create composite materials with increased conductivities and/or novel functionalities (e.g., pseudocapacitance), since these techniques are not limited by the electrospinnability of the precursor solutions. A wide range of new chemistries and even micro- or nano-textures could be incorporated into the electrospun carbon nanofiber webs through the use of surface modification techniques such as click chemistry, electrodeposition or electropolymerization of redox-active species, or layer-by-layer deposition of conductive components (i.e., carbon nanotubes with positive and negative surface charges).

Specific surface areas of porous carbon materials are closely related to their electrochemical performance in both supercapacitor devices and lithium ion batteries. High surface areas, which accelerate ion transport, can accommodate large quantities of ions as well as improve rate capability. As mentioned earlier, with catalysts such as $ZnCl_2$,

a decrease in carbon fiber diameters with a corresponding increase in surface area has been achieved.[51] The addition of cellulose acetate into PAN/DMF solutions resulted in an increase in surface area from 740 to 1160 m^2/g and therefore improved capacitance from 141 to 245 F/g at a current density of 1 mA/cm^2.[53] The composition of the precursor solutions as well as the nature of the carbon precursor itself could have significant effects on the carbonization process. Another possible opportunity lies in utilizing different catalysts to modulate the thermal treatment process, and to study the effects of catalysts on surface area of the resulting carbon nanofiber webs. Highly porous fibers with enhanced surface areas might be created using novel templating methods such as use of a PAN-*b*-PMMA block copolymer, with the capability to burn off the MMA component during carbonization, therefore creating unusual types of pores inside of the fibers.

Another interesting aspect of nanocarbon-based energy materials is control of ion adsorption ability and Li^+ storage capacity through manipulation of pore structures on the carbon surface. Different types of pores can be generated in the electrospun carbon nanofiber webs: large inter-fiber spaces, macropores (> 50 nm in average diameters), mesopores (2 – 50 nm in average diameters), and micropores (< 2 nm in average diameters). The size and structure of large inter-fiber spaces determine the porosity and bulk density of the electrospun webs, which is important for the volumetric storage capacity. In addition, the characteristic length scale of ion diffusion pathways is related to the dimension of these large inter-fiber spaces. Therefore optimization of web density and inter-fiber distance could lead to improved rate capability. However, the sizes of these large inter-fiber spaces tend to correlate with fiber diameter, so that these two properties are difficult to control independently. Hot-press treatment during stabilization

and *in situ* control of pressure applied to the precursor polymer web during carbonization can be used to modulate the size of large inter-fiber spaces in the resultant carbon fiber webs.

It has been shown that the formation of micropores on the fiber surface could lead to good rate performance.[47,49] To control the extent of micropore formation in individual fibers, conventional activation steps (e.g, using steam, base and acid as the activation agents) have been utilized, since the micropores are formed during the evolution of different gaseous species such as CO, CO_2 and various types of hydrocarbons, which depends strongly upon the thermal treatment conditions. Mesopores and macropores are often introduced to carbon fibers in order to enhance surface area, in most cases through the use of an additional carbon precursor that acts as a pore-former or through the inclusion of some templates or sacrificial materials in the electrospinning solution. In addition, hierarchical pore structure can be introduced to electrospun fiber webs through the use of electrospinning solutions composed of polymer A/polymer B/solvent/non-solvent.[87] The mesopores formed inside the fibers themselves are generated as the solution phase-separates into polymer-rich and solvent-rich domains during the electrospinning process.

Another aspect of electrospun carbon fiber-based energy materials that has seen less attention to date is the mechanical properties of the free-standing webs, which generally need to be enhanced because carbon fibers are often brittle and must be handled with caution. This is of practical importance if flexible, printable and wearable carbon nanofiber-based energy storage devices are to be integrated into smart clothing, sensors, wearable electronics and gene/drug delivery systems. In addition, theoretical guidance is

scarce for the design of electrospun carbon nanofibers, in particular when combined with other materials to give new functionalities. Mathematical modeling and simulation tools developed for porous electrode thermodynamics and kinetics could be adapted to describe the electrochemical properties of electrospun carbon nanofiber webs.

Several challenges still remain to be overcome before industrial scale usage of this technique is realized. There are limitations on the types of materials that can be fabricated by electrospinning, and it is sometimes difficult to formulate solutions with the desired chemical properties that are at the same time spinnable into uniform fibers of the desired size and morphology. The carbonization processes involve complex physical and chemical changes, and the effects of the precursor and the solution composition on the development of graphiteic structures are not fully understood. To optimize energy storage capability, precise control of fiber diameters, porosity, and distribution of active components in the fibers is of immediate importance. Controlled synthesis and modification techniques for carbon nanofibers with enhanced specificity and high flexibility might be necessary to improve electrochemical performance. Additional challenges are associated with scale-up of the electrospinning technique and down-stream processing, which are essential for the use of electrospun carbon fibers in large scale manufacturing of energy storage devices. Multi-jet nozzles or free surface electrospinning[34] are possible strategies to increase productivity and achieve large scale nanofiber production.

6. Conclusion

Among various fabrication methods for ultrafine carbon fibers, the technique of electrospinning followed by thermal treatment is undergoing intense scrutiny for energy-related applications. This technique provides relatively flexible control over morphology, degree of graphitization, and chemical functionality of the resulting 1D nanostructured carbon fibers. Therefore optimization of the electrochemical properties of electrospun carbon fibers for the development of advanced energy storage devices is an area ripe for development. Tables 1 and 2 summarize the recent advances in using electrospun carbon fibers as electrode materials for supercapacitors and lithim-ion batteries. We have discussed briefly the principles of the electrospinning/thermal treatment method as well as the characterization techniques for the resultant carbon fibers. For the applications of electrospun carbon fibers to supercapacitor devices, increasing conductivity and surface area are the most frequently adopted strategies to improve the electrocapactive performance. In LIB applications, most published accounts report electrospun carbon fibers serving as supports or structural buffers for Si or Sn, which have much higher theoretical values for lithium ion storage than does graphite. These composite fibers have been in the forms of either core (Si/Sn)-shell (carbon) fibers, or Si/Sn nanoparticles deposited on the carbon fiber surfaces. Future generations of supercapacitors are expected to come close to current lithium-ion batteries in terms of high energy density maintained at high power density. This may be achieved by discovering new materials that combine double layer capacitance and pseudocapacitance, and by developing hybrid systems. On the other hand, the cycling performance of lithium ion batteries is expected to improve significantly, to a level approaching the cycling stability of supercapacitors, with the objective of retaining the initial capacity even after more than 1000 charge/discharge

cycles. Good progress toward this goal has been made, but further optimization by developing structural buffers with well-defined nano-scale geometries is waranted.

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