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Perspective

Graphene fiber based supercapacitors: Strategies and perspective toward high performances

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ABSTRACT

Modern wearable electronics are thirsty for flexible, lightweight energy storage and supply devices. Flexible fiber-shaped supercapacitors, possess good flexibility, high power density, fast charging capability and long cycle life, becoming a promising option for wearable devices. The past decade has witnessed the emergence of graphene fiber based supercapacitors (GFSCs) as one of the most active vicinity in fiber-supercapactiors, for their excellent properties including high surface area, chemical stability, excellent electrical conductivity, lightweight and mechanical properties. In this perspective, we introduced the basic energy storage mechanisms of GFSCs, followed by the analysis in improving their overall performances, recent advances, and a conclusive discussion on the challenges and opportunities.

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1. Introduction

Increasing demands for high-tech electronic products drive very impressive progresses in developing flexible, lightweight and wearable electronic devices, such as electronic skins, smart clothes, displays, bendable smart phones for applications from sport products to health monitoring over past decades. A power storage and supply system with high capacitance and fast charging rate is usually required to support the daily working of these wearable electronics. Due to the high power density, fast charging capability and long cycle life, flexible supercapacitors (SCs) are one of promising power sources for portable and wearable devices [1]. They can fill the gap between batteries and conventional capacitors, stemming from a higher power density than batteries and fuel cells, and a higher energy density than conventional capacitors [2].

The new generation of flexible SCs has to be lightweight, flexible and wearable while retaining their electrochemical capability

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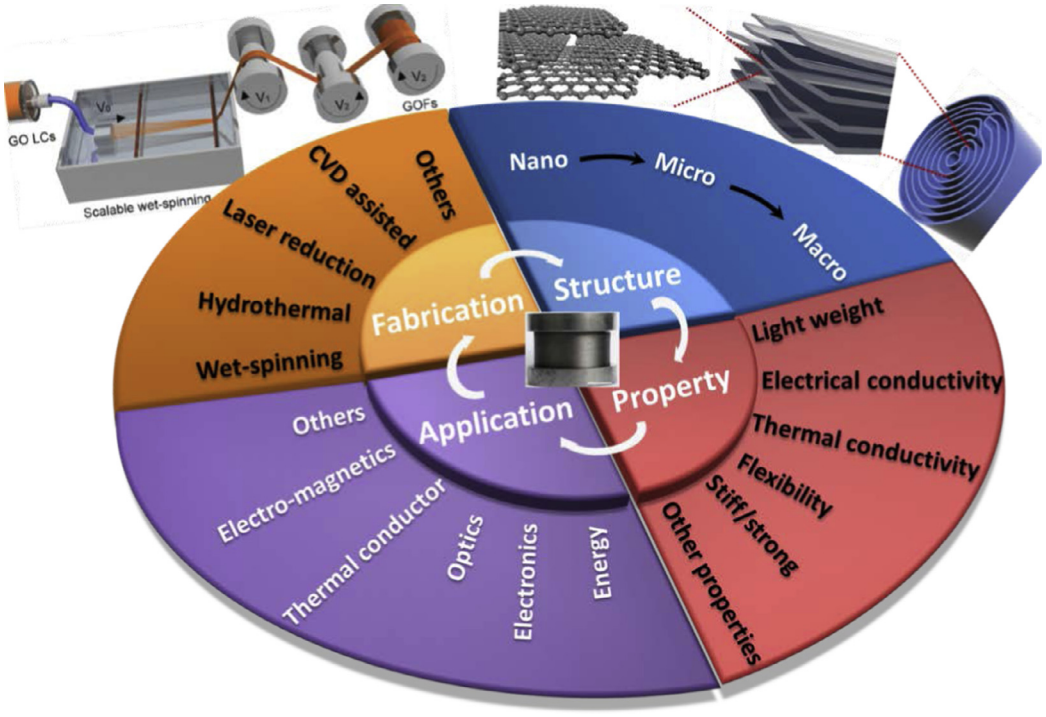

Fig. 1. Fabrication [50], structure [50], performance and applications of GFs.

while deforming. One of the key challenges of flexible SCs is the design and fabrication of flexible electrodes with both high energy and power density. Integrating electrochemical active materials into flexible fibers, which can be easily integrated into woven textiles or nonwoven fabrics, becomes one of effective strategies to address the above issue [2–7]. Compared to the conventional polymer fibers and metal wires, graphene fibers (GFs), possess various excellent properties including high surface area, chemical stability, excellent electrical conductivity, lightweight and mechanical properties, and thus were particularly desirable as electrode backbones for supercapacitors (Fig. 1) [7–10]. The greatly developed manufacturing technique of GFs, such like the wet-spinning approach, hydrothermal strategy, laser reduction technique, CVD-assisted process, electrophoretic self-assembly method, hard-template method, etc, provided the solid materials foundation for the development of GFSCs [8–10].

Despite a large number of fundamental researches in GFSCs, energy densities were still low, far poorer than those of batteries. Design of GFSCs with high energy density and electrochemical stability at dynamic states is in need. For a supercapacitor, the energy density E is calculated by the equation of $E = 1/2CU^2$, where C represents the capacitance of active materials/electrodes/whole devices and U is term to the working voltage window. From this fundamental correlation, the enhancement of E is assorted to the improvement of C and/or U. In this perspective we focus in particular on strategies to improve the overall performance of GFSCs (Fig. 2).

2. Strategies to improve capacitance performance

The energy storage of neat graphene fiber based FSCs is dominated by an electrostatical accumulation of positive and negative charges at the interface between electrode surface and electrolytes, called as electrical double-layer capacitors (EDLCs) mechanism [11]. Depending on the preparation approaches applied, most of generated GFs are partially chemically reduced and have some functional groups left. In these cases, a reversible surface or near surface faradic reaction between functional groups and electrolyte can take place, namely pseudocapacitance, but its contribution to energy density increase accounts less due to the limited amount of active sites for redox reactions and the increased electrical resistance along fiber axial [12–14]. For EDLC-type GFSCs, the restacking of graphene sheets hampers to achieve the high specific surface area (SSA) and limits the specific capacitance and energy density. Meanwhile, the stacking of graphene sheets has a great contribution for the fine electrical and mechanical properties of fibers [15–17]. Therefore, we need to face the challenge that how to control the assembled microstructure of graphene sheets in GFs and balance the mechanical attribute and capacitance performance.

Recently, several strategies were applied to achieve the balance between mechanical attribute and capacitance performance for GFSCs (Table 1). (i) Effective utilization of SSA of graphene sheets with the inner fiber structure design without destroying the electrical conductive pathway [18–20], like coaxial structures; (ii) Integration of porous carbon materials onto GF surfaces or production of porous surface on GFs to provide larger electrolyte accessible SSA and thus the higher charge absorption capability [21–24]; (iii) Addition of conductive spacers, like CNTs [25–27]. (iv) Heteroatoms doping (mostly nitrogen) to provide enhanced electrolyte wettability of carbon with larger SSA or sometimes pseudocapacitance [28,29].

EDLCs based GFSCs generally exhibit constant energy densities for all timescales because there is no irreversible redox reactions occurring but their total stored energy is low. Pseudocapacitors, on the other hand, function via reversible redox reactions take place and are charge-discharged fast enough as EDLCs with significantly higher capacitances [30]. However, most pseudocapacitive materials are not or less electrically conductive, greatly limiting their real applications in power storage and supply. Incorporating high energy density pseudocapacitive materials into high electrically conductive GFs backbones can result dramatic improvement of the overall performance of GFSCs. Various pseudocapactive electrode materials (Table 1), were utilized to fabricate GFSCs with high performance and flexibility, including

Table 1. Summary of the performance of graphene fiber based supercapacitors.

Electrodes	Electrolytes	Type	Voltage (V)	Capacitance	E_V	P_V	Cycling life -Cs retention	Ref.
RGO-GO-RGO fiber	$EMIMBF_4$	all in one	1.0	[c]0.45 mF cm^{-2}@ 0.2 mA cm^{-2}	[c]2–5.4 × 10^{-4} Wh cm^{-2}	[c]3.6-9 × 10^{-2} W cm^{-2}	160 – 80%	[15]
RGO-GO-RGO series	none	all in one	0.8	[c]14.3 mF cm^{-2}@50 mA cm^{-3}			1000 – 97%	[16]
RGO fiber	PVA/H_3PO_4	parallel	1.0	[b]3.3 mF cm^{-2}@0.1 mA cm^{-2} (3.8 F cm^{-3})			5, 000 – 100%	[17]
Graphene yarn	1 M H_2SO_4	consecutive	1.0	[b]09 F g^{-1}@ 1 A g^{-1}	[b]14 × 10^{-3} Wh g^{-1}	[b]25 W g^{-1}	5000 – 100%	[18]
GF	PVA/H_2SO_4	parallel	1.0	[b]185 F g^{-1}@0.244 A cm^{-3} (226 mF cm^{-3})	[b]7.03 × 10^{-3} Wh cm^{-3} [b]5.76 × 10^{-3} Wh g^{-1}	[b]5.77 × 10^{-2} W cm^{-3} [b]4.7 × 10^{-2} W g^{-1}	1000 – 92%	[19]
GF	PVA/H_2SO_4	coaxial	0.8	[c]205 mF cm^{-2}@10 mV s^{-1} (182 F g^{-1})	[c]1.75 × 10^{-5} Wh cm^{-2} [c]1.55 × 10^{-2} Wh g^{-1}	[c]8.19 × 10^{-4} W cm^{-2}	10,000 – 100%	[20]
Porous graphene ribbons	PVA/H_2SO_4	parallel	0.8	[b]208.7 F g^{-1}@0.1 A g^{-1} (78.3 mF cm^{-2})			5000 – 99%	[21]
Vertical graphene ribbons(VGR)	1 M Na_2SO_4	–	1.0	[b]234.8 F cm^{-3}@2 mV s^{-1}			10,000 – 96%	[22]
GF@3D-G	PVA/H_2SO_4	twist	0.8	[b]1.2–1.7 mF cm^{-2}@17 – 424.6 μA cm^{-2} (25-40 F g^{-1})	[b]0.4–1.7 × 10^{-7} Wh cm^{-2}	[b]6–100 × 10^{-6} W cm^{-2}		[23]
GF-AC	PVA/H_2SO_4	twist	0.8	[c]27.6 F cm^{-3}@13 mA cm^{-3} (43.8 F g^{-1})	[c]2.5 × 10^{-3} Wh cm^{-3}	[c]5 × 10^{-3} W cm^{-3}	10,000 – 90%	[24]
GF-CNT	PVA/H_3PO_4	parallel	0.8	[b]31.5 F g^{-1}@0.04 A g^{-1} (4.97 mF cm^{-2})			5000 – 100%	[25]
GF-CNT	PVA/LiCl	parallel	0.8	[b]2.38 mF cm^{-2}@10 mV s^{-1}			6000 – 100 ± 4%	[26]
GF-CNT	PVA/H_3PO_4	parallel	0.8	[c]38.8 F cm^{-3}@50 mA cm^{-3}	[c]3.4 × 10^{-3} Wh cm^{-3}	[c]0.7 W cm^{-3}	10,000 – 93%	[27]
N-doped RGO-SWCNT	PVA/H_3PO_4	parallel	1.0	[b]300 F cm^{-3}@26.7 A cm^{-3} (116.3 mF cm^{-2})	[c]6.3 × 10^{-3} Wh cm^{-3}		10,000 – 93%	[28]
N-doped GF	PVA/H_3PO_4	parallel	0.8	[c]1132 mF cm^{-2}@0.1 mA cm^{-2}			10,000 – 97%	[29]
N-doped GF	$EMIBF_4$ /PVDF-HFP	parallel	3	[c]306.3 mF cm^{-2}@1 mA cm^{-2}	[c]4.7-9.6 × 10^{-5} Wh cm^{-2}	[c]1.5-15 W cm^{-2}	10,000 – 97%	[29]
GF-MnO_2	PVA/H_3PO_4	parallel	1.0	[b]42 F cm^{-3}@10 mV s^{-1}	[b]1.46 × 10^{-6} Wh cm^{-2}	[b]2.94 × 10^{-3} W cm^{-2}	10,000 – > 80%	[31]
MnO_2/G/GF	PVA/H_2SO_4	twist	0.8	[b]9.1-9.6 mF cm^{-2}@100 mV s^{-1} (34-36 F g^{-1})			1000 – 100%	[32]
GF-MnO_2	PVA/H_3PO_4	twist	0.8	[b]66.1 F cm^{-3}@60 mA cm^{-3} (82.6 mF cm^{-2})	[b]5.8 × 10^{-3} Wh cm^{-3}	[b]0.51 W cm^{-3}	10,000 – 96%	[33]
GF-Mn_3O_4	PVA/H_3PO_4	twist	0.8	[b]45.5 F cm^{-3}@50 mA cm^{-3}	[b]4.05 × 10^{-3} Wh cm^{-3}	[b]0.27 W cm^{-3}	10,000 – > 80%	[34]
GF-Bi_2O_3	PVA/H_3PO_4	parallel	1.0	[b]69.3 mF cm^{-2}@10 mV s^{-1} [c]17.3 mF cm^{-2}@10 mV s^{-1}			1000 – 100%	[35]
GF-MXene	PVA/H_3PO_4	parallel	0.8	[b]372.2 mF cm^{-2}@10 mV s^{-1} (586.4 F cm^{-3})	[b]1.3 × 10^{-2} Wh cm^{-3}	[b]0.59 W cm^{-3}	3000 – 95%	[36]
GF-MoS_2	PVA/H_2SO_4	twist	1.0	[b]30 mF cm^{-3}@0.1 μA			1000 – 80%	[37]
GF-MoS_2	PVA/H_3PO_4	unknown	0.8	[b]598 mF cm^{-2}@ 5 mV s^{-1} (368 F cm^{-3}, 214 F g^{-1})	[c]1.28 × 10^{-2} Wh cm^{-3}		8000 – 80%	[38]
GF-PPy	PVA-H_2SO_4	twist	0.8	[b]107.2 F cm^{-3}@0.24 mA cm^{-2}	[b]6.6-9.7 × 10^{-6} Wh cm^{-2}		1000	[39]
GF-PANI	PVA/H_3PO_4	parallel	1.0	[b]66.6 mF cm^{-2}@0.1 mA cm^{-2} (79.1 F cm^{-3})				[17]
RGF/ PEDOT:PSS	PVA/H_3PO_4	coaxial	0.8	[b]304.5 mF cm^{-2}@0.08 mA cm^{-2} (143.3 F cm^{-3}, 63.1 F g^{-1})	[b]2.71 × 10^{-5} Wh cm^{-2}	[b]6.65 × 10^{-5} W cm^{-2}	10,000 – 96%	[40]
GF/CNTs/PEDOT:PSS@CMC	PVA/H_3PO_4	coaxial	1.0	[b]396.7 mF cm^{-2}@0.1 mA cm^{-2}	[b]5.5-3.9 × 10^{-5} Wh cm^{-2}	[b]1-10 × 10^{-5} W cm^{-2}	5000 – 90%	[41]
RGO + CNT@CMC	PVA/H_3PO_4	coaxial	0.8	[b]158 mF cm^{-2} @0.1 mA cm^{-2} (177 F cm^{-3})	[b]3.84 × 10^{-6} Wh cm^{-2} [c]3.5 × 10^{-3} Wh cm^{-3}		2000 – 100%	[42]
GF-PVA	PVA/H_2SO_4	twist	0.8	[b]172 F g^{-1}@0.1 A g^{-1} (191 F cm^{-3})	5.97 × 10^{-6} Wh cm^{-3} 5.32 × 10^{-6} Wh g^{-1}	2.69 × 10^{-5} W cm^{-3} 2.39 × 10^{-5} W g^{-1}	1000 – 85%	[43]
GF@$NiCo_2S_4$//GF	PVA/KOH	parallel	1.5	[a]39.4 F cm^{-3} @ 175.7 mA cm^{-3}	[a]1.23 × 10^{-2} Wh cm^{-3}	[a] 1.6 W cm^{-3}	2000 – 92%	[44]
GF-MoO_3//GF-MnO_2	PVA/H_3PO_4	twist	1.6	[c]53.5 F cm^{-3}@100 mA cm^{-3}	[c]1.82 × 10^{-2} Wh cm^{-3}	[c]7.64 × 10^{-2} W cm^{-3}	3000 – 97%	[45]
MoS_2-rGO-MWCNT// rGO-MWCNT	PVA/H_2SO_4	parallel	1.4	[c]5.2 F cm^{-3}@0.16 A cm^{-3}	[c]10^{-3} Wh cm^{-3}		7000 – 100%	[46]
VGR//VGR/MnO_2	PVP/Na_2SO_4	unknown	1.8	[c]12.8 F cm^{-3}@75 mA cm^{-3}	[c]5.7 × 10^{-3} Wh cm^{-3}		10,000 – 88%	[22]
GF-MnO_2//GF-CNT	PVA/LiCl	twist	1.6	[c]23.6 mF cm^{-2}@0.5 mA cm^{-2}	[c]8.0 × 10^{-6} Wh cm^{-2}		8000 – 93%	[47]

[a] Active materials.
[b] Electrode.
[c] Devices or no superscript indicates the data reported without detailed descriptions of their calculation methods.

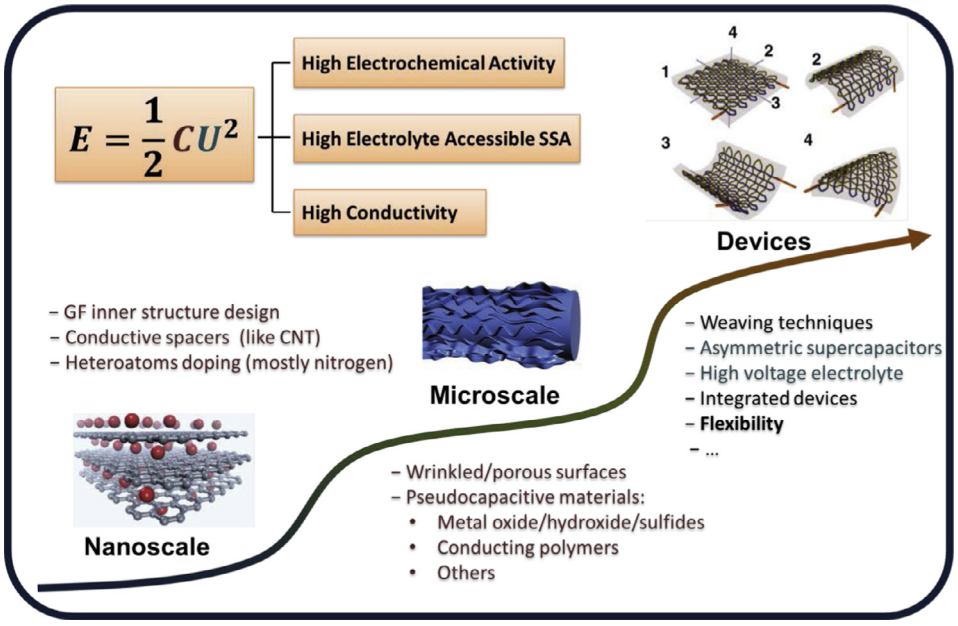

Fig. 2. Energy storage mechanism and improvement strategies for high performance GFSCs [42,50,51].

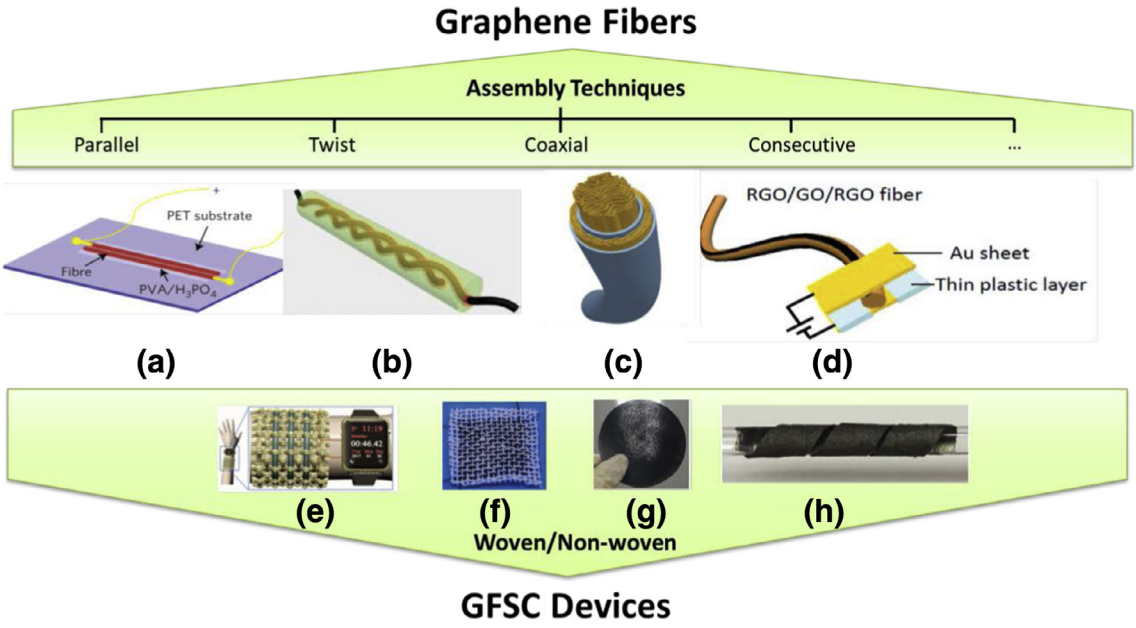

Fig. 3. Assembly techniques for GFSC devices: (a) parallel type [28]; (b) twit type [42]; (c) coaxial type [20]; (d) consecutive type [15]; (e, f) Woven GF textiles [29,42]; (g, h) Non-woven GF fabrics [48,49].

metal oxide/hydroxide/nitrides/sulfides (like MnO_2 [31–33], Mn_3O_4 [34], Bi_2O_5 [35], MXene [36], WS_2 [37,38]), electrically conducting polymers (like polypyrrole (PPy) [39], polyaniline (PANI) [17], poly(3,4-ethylenedioxythiophene) (PEDOT) [40,41]), sodium carboxymethyl cellulose (CMC) [42], polyvinyl alcohol (PVA) [43], etc. Despite so, low electrochemical stability and relatively short cycling life still challenge for pseducapacitive GFSCs due to structural degradations through the redox process.

3. Strategies to widen voltage window

Asymmetric devices were fabricated by combining a capacitive GF with either a pseudocapacitive electrode (called as asymmetric supercapcitors) or a lithium insertion electrode (namely hybrid supercapcitors), aiming for both high power density and high energy density [21,44–47]. The working voltage window can be widened to 1.5–1.8 V from 0.8–1.0 V of symmetric SCs via asymmetric matches and so does capacitance.

The voltage window of GFSCs was greatly limited by currently used electrolytes (mostly PVA based gel), which is hard to exceed 2.0 V. In this regard, developing new solid state electrolytes with wider working potential window and high ion conductivity seems the emerging direction toward ever-improved energy densities for GFSCs [29].

4. Assembly techniques of graphene giber supercapacitor devices

In addition to the GF micro-structure design, the capacitance of active materials, and the type of electrolytes, the assembly

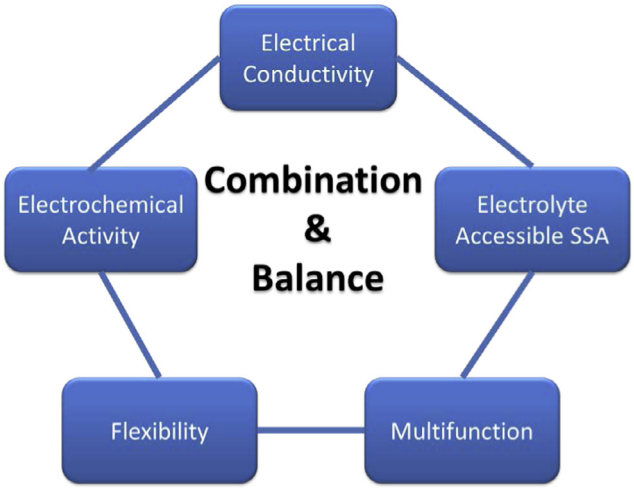

Fig. 4. Parameters should be combined and balanced for next-generation GFSCs.

technique for GFSC devices is also a key technique for high performance GFSCs. Several types of assembled GFSCs were reported, including parallel [17,19,21,25–28,30,31,35,36,44,46], twist [23,24,32–34,37,39,43,45,47], coaxial [20,40–42], and other consecutive types [15,16,18] (Fig. 3). Parallel type normally needs substrates to support two parallel electrodes which would induce low overall specific performance. The distance between two electrodes on the substrate can be carefully controlled to avoid short circuit. On the contrast, the specific performance of twist type GFSCs can be improved without introducing extra substrate but short circuit can also easily formed due to the close twisted electrodes. Coaxial type GFSCs, composed of GF core and shell electrode separated by electrolyte, can effectively utilize the electrode material with enhanced performance. However, direct contact between two electrodes, the chief culprit for short circuit, should be avoided through the whole length of devices.

5. Conclusions and perspective

GFSCs have developed as a promising candidate for the fiber supercapacitors, demonstrated by their fascinating performances in high capacitances, good flexibility and easy to integrate with textiles. Recent researches have concluded the fundamental notion on the structural design and the relationship between structure and property of GFSCs. The overall capacitance performance of GFSCs is mainly determined by the electrolyte accessible SSA, the conductivity, and the capacitive properties of electrode materials introduced into GFs, the assembly technique of FSC devices. With proper design on above mentioned parameters along with widened working voltage window, great energy storage performance improvement of GFSCs can be expected (Fig. 4).

For practical applications, energy density in fact is not the sole aim for GFSC devices design and optimization. There are more other metrics have to be considered for FSCs performance evaluation, such like power density, rate capability, and cycle stability, bending/stretching/weaving/twisting properties, etc. Generally, EDLCs based GFs provide high power density and long cycling life, pseudocapcitively activated GFSCs hold higher energy density with sacrificing on cycling stability and life, while asymmetric devices aim for both high energy density and power density, giving rise to abundant choices to meet the practical demands for GFSCs.

The development of GFSCs is still in its early stage. Despite various possible strategies were provided to get high performance GFSCs, many technique challenges still exist in fundamental research and practical applications, including:

(1) How to realize larger SSA without enlarging the electrical resistance for EDLCs based GFSCs by controlling the conformation of graphene sheets;
(2) How to effectively incorporate pseudocapacitive materials into graphene fiber backbones with both high conductivity and long cycling life;
(3) How to design electrolytes with large working voltage window and effectively accessing into electrodes with high ion conductivity;
(4) How to push the research on single fiber devices to the scalable fabrication of bundles, textile and even cloth devices;
(5) How to integrate multifunctional properties into one GFSCs to fulfill the demands for complex tasks;
(6) How to effectively integrate GFSCs with other electrics for smart applications;
(7) etc.

To solve these problems, cooperation between researchers from various fields including materials science, physics, electrochemistry, electronics, textile science and engineering is required. We hope this perspective can inspire new sight in this field in order to promote the development of GFSCs for practical applications.

Acknowledgments

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References

[1] W. Liu, M.-S. Song, B. Kong, Y. Cui, Adv. Mater. 29 (2017) 1603436.
[2] D.S. Yu, Q.H. Qian, L. Wei, W.C. Jiang, K.L. Goh, J. Wei, J. Zhang, Y. Chen, Chem. Soc. Rev. 44 (2015) 647–662.
[3] S.T. Senthilkumar, Y. Wang, H.T. Huang, J. Mater. Chem. A 3 (2015) 20863–20879.
[4] W. Weng, P.N. Chen, S.S. He, X.M. Sun, H.S. Peng, Angew. Chem. Int. Ed. 55 (2016) 6140–6169.
[5] U. Gulzar, S. Goriparti, E. Miele, T. Li, G. Maidecchi, A. Toma, F. De Angelis, C. Capiglia, R. Zaccaria, J. Mater. Chem. A 4 (2016) 16771–16800.
[6] F.C. Meng, Q.W. Li, L.X. Zheng, Energy Storage Materials 8 (2017) 85–109.
[7] H. Sun, Y. Zhang, J. Zhang, X.M. Sun, H.S. Peng, Nat. Rev. Mater. 2 (2017) 17023.
[8] F.C. Meng, W.B. Lu, Q.W. Li, J.-H. Byun, Y. Oh, T.-W. Chou, Adv. Mater. 27 (2015) 5113–5131.
[9] J. Li, X.K. Huang, L.F. Cui, N. Chen, L.T. Qu, Progr. Nat. Sci.: Mater. Inter. 26 (2016) 212–220.
[10] L.L. Chen, Y. Liu, Y. Zhao, N. Chen, L.T. Qu, Nanotechnology 27 (2016) 032001.
[11] W. Lv, Z.J. Li, Y.Q. Deng, Q.-H. Yang, F.Y. Kang, Energy Storage Mater. 2 (2016) 107–138.
[12] S. Kerisit, B. Schwenzer, M. Vijayakumar, J. Phys. Chem. Lett. 5 (2014) 2330–2334.
[13] S.-W. Park, A.D. DeYoung, N.R. Dhumal, Y. Shim, H.J. Kim, Y.J. Jung, J. Phys. Chem. Lett. 7 (2016) 1180–1186.
[14] K. Xu, X. Ji, C. Chen, H.Z. Wan, L. Miao, J.J. Jiang, Electrochimica Acta 166 (2015) 142–149.
[15] Y. Hu, H. Cheng, F. Zhao, N. Chen, L. Jiang, Z. Feng, L. Qu, Nanoscale 6 (2014) 6448–6451.
[16] Y. Liang, Z. Wang, J. Huang, H. Cheng, F. Zhao, Y. Hu, L. Jiang, L. Qu, J. Mater. Chem. A 3 (2015) 2547–2551.
[17] T.Q. Huang, B.N. Zheng, L. Kou, K. Gopalsamy, Z. Xu, C. Gao, Y.N. Meng, Z.X. Wei, RSC Adv. 3 (2013) 23957–23962.
[18] S.H. Aboutalebi, R. Jalili, D. Esrafilzadeh, M. Salari, Z. Gholamvand, S. Aminorroaya Yamini, K. Konstantinov, R.L. Shepherd, J. Chen, S.E. Moulton, P.C. Innis, A.I. Minett, J.M. Razal, G. G. ACS Nano 8 (2014) 2456–2466.
[19] S. Chen, W. Ma, Y. Cheng, Z. Weng, B. Sun, L. Wang, W. Chen, F. Li, M. Zhu, H.M. Cheng, Nano Energy 15 (2015) 642–653.
[20] X. Zhao, B. Zheng, T. Huang, C. Gao, Nanoscale 7 (2015) 9399–9404.
[21] G. Huang, C. Hou, Y. Shao, B. Zhu, B. Jia, H. Wang, Q. Zhang, Y. Li, Nano Energy 12 (2015) 26–32.
[22] L.Z. Sheng, T. Wei, Y. Liang, L.L. Jiang, L.T. Qu, Z.J. Fan, Small 13 (2017) 1700371.
[23] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, Adv. Mater. 25 (2013) 2326–2331.
[24] W. Ma, S. Chen, S. Yang, W. Chen, W. Weng, M. Zhu, ACS Appl. Mater. Interfaces 8 (2016) 14622–14627.

[25] H. Sun, X. You, J.E. Deng, X.L. Chen, Z.B. Yang, J. Ren, H.S. Peng, Adv. Mater. 26 (2014) 2868–2873.
[26] K.M. Kim, J.A. Lee, H.J. Sim, K.-A. Kim, R. Jalili, G.M. Spinks, S.J. Kim, Nanoscale 8 (2016) 1910–1914.
[27] Y. Ma, P. Li, J.W. Sedloff, X. Zhang, H. Zhang, J. Liu, ACS Nano 9 (2015) 1352–1359.
[28] D.S. Yu, K. Goh, H. Wang, L. Wei, W.C. Jiang, Q. Zhang, L.M. Dai, Y. Chen, Nat. Nanotechnol. 9 (2014) 555–562.
[29] G. Wu, P. Tan, X. Wu, L. Peng, H. Cheng, C.-F. Wang, W. Chen, Z. Yu, S. Chen, Adv. Funct. Mater. 27 (2017) 1702493.
[30] V. Augustyn, P. Simon, B. Dunn, Energy Environ. Sci. 7 (2014) 1597–1614.
[31] X. Li, T. Zhao, Q. Chen, P. Li, K. Wang, M. Zhong, J. Wei, D. Wu, B. Wei, H. Zhu, Phys. Chem. Chem. Phys. 15 (2013) 17752–17757.
[32] Q. Chen, Y.N. Meng, C.G. Hu, Y. Zhao, H.B. Shao, N. Chen, L.T. Qu, J. Power Sources 247 (2014) 32–39.
[33] W. Ma, S. Chen, S. Yang, W. Chen, Y. Cheng, Y. Guo, S. Peng, S. Ramakrishna, M. Zhu, J. Power Sources 306 (2016) 481–488.
[34] S.B. Chen, L. Wang, M.M. Huang, L.P. Kang, Z.B. Lei, H. Xu, F. Shi, Z.-H. Liu, Electrochimica Acta 242 (2017) 10–18.
[35] K. Gopalsamy, Z. Xu, B. Zheng, T. Huang, L. Kou, X. Zhao, C. Gao, Nanoscale 6 (2014) 8595–8600.
[36] Q. Yang, Z. Xu, B. Fang, T. Huang, S. Cai, H. Chen, Y. Liu, K. Gopalsamy, W. Gao, C. Gao, J. Mater. Chem. A (2017), doi:10.1039/C7TA07999K.
[37] G.Z. Sun, J.Q. Liu, X. Zhang, X.W. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, Angew. Chem. Int. Ed. 53 (2014) 12576–12580.
[38] B. Wang, Q. Wu, H. Sun, J. Zhang, J. Ren, Y. Luo, M. Wang, H. Peng, J. Mater. Chem. A 5 (2017) 925–930.
[39] X. Ding, Y. Zhao, C. Hu, Y. Hu, Z. Dong, N. Chen, Z. Zhang, L. Qu, J. Mater. Chem. A 2 (2014) 12355–12360.
[40] G. Qu, J. Cheng, X. Li, D. Yuan, P. Chen, X. Chen, B. Wang, H. Peng, Adv. Mater. 28 (2016) 3646–3652.
[41] S. Cai, T. Huang, H. Chen, M. Salman, K. Gopalsamy, C. Gao, J. Mater. Chem. A (2017), doi:10.1039/C7TA07937K.
[42] L. Kou, T.Q. Huang, B.N. Zheng, Y. Han, X.L. Zhao, K. Gopalsamy, H.Y. Sun, C. Gao, Nat. Commun. 5 (2014) 3754.
[43] S. Chen, W. Ma, H. Xiang, Y. Cheng, S. Yang, W. Weng, M. Zhu, J. Power Sources 319 (2016) 271–280.
[44] W. Cai, T. Lai, J. Lai, H. Xie, L. Ouyang, J. Ye, C. Yu, Sci. Rep. 6 (2016) 26890.
[45] W. Ma, S. Chen, S. Yang, W. Chen, W. Weng, Y. Cheng, M. Zhu, Carbon 113 (2017) 151–158.
[46] G. Sun, X. Zhang, R. Lin, J. Yang, H. Zhang, P. Chen, Angew. Chem. Ed. Int. 127 (2015) 4734–4739.
[47] B. Zheng, T. Huang, L. Kou, X. Zhao, K. Gopalsamy, C. Gao, J. Mater. Chem. A 2 (2014) 9736–9743.
[48] Z. Li, Z. Xu, Y.J. Liu, R. Wang, C. Gao, Nat. Commun 7 (2016) 13684.
[49] Z. Li, T.Q. Huang, W.W. Gao, Z. Xu, D. Chang, C.X. Zhang, C. Gao, ACS Nano (2017), doi:10.1021/acsnano.7b05092.
[50] Z. Xu, Y.J. Liu, X.L. Zhao, L. Peng, H.Y. Sun, Y. Xu, X.B. Ren, C.H. Jin, P. Xu, M. Wang, C. Gao, Adv. Mater. 28 (2016) 6449–6456.
[51] Y.J. Liu, Z. Xu, J.M. Zhan, P.G. Li, C. Gao, Adv. Mater. 28 (2016) 7941–7947.