Review of Recent Advancements Made In Flexible Energy Storage Devices

H Kumar¹, K Kumar ² and H K Bhardwaj ³
¹Department of Mechanical Engineering, National Institute of Technology, Delhi, India. Email: hriishkec@gmail.com
²Department of Mechanical Engineering, Meerut Institute of Engineering and Technology, Meerut, India. Email: krishna.kumar@miet.ac.in
³Department of Mechanical Engineering, Meerut Institute of Engineering and Technology, Meerut, India. Email: harsh.bhardwaj@miet.ac.in

ABSTRACT: There are unlimited potentials have been seen in the fields of condition health monitoring, wearable consumer electronics and human motion tracking for the design of soft exosuits. Energy storage devices are the key element in all above mentioned fields, which can be of high capacitance, light weighted and flexible too. Fiber based supercapacitors are based fit to these. In last few decades’ different kind of fiber based supercapacitors have been developed, among them carbon nano-tube (CNT) based fiber electrodes showed that their capacitance, energy density and cycle life is higher as compared to conventional wire based electrodes. In this paper our aim is to review the advances made in the field of different type of fiber based supercapacitors.

Keywords: Flexible energy storage devices, supercapacitors, carbon nano-tubes.

1. INTRODUCTION

In supercapacitors energy is stored within the space in-between an electrode and the electrolyte. It has been seen that the conversion of a simple cloth fabric into energy storing supercapacitor is an advancement. A one-step hydrothermal synthesis process is used on natural cotton thread by Zhou et al [1] to develop a multi-walled carbon nanotubes cotton thread. Because of their good electrochemical and mechanical properties, the multi-walled carbon nanotubes supercapacitors, which were cotton thread based, can be directly knitted into fabrics without changing their parent structures. Fiber electrodes (GHs/MWCNTs-CT) and polyvinyl alcohol-H3PO4 gel electrolyte based supercapacitors exhibit high capacitive performance and long cycle life (95.51% capacitance performance after 80000 charge-discharge cycles).

The supercapacitors, which we used in apparel electronics, faces irreversible deformation due to long term local stress concentration which lead to structural fatigue. Huang et al [2] first time developed wire shaped shape memory functions embedded supercapacitors called shape memory supercapacitor (SMSC). SMSC’s remember their predesigned shape, when they reached their trigger temperature they restore serious plastic deformations and regain their original shapes within seconds. This advance feature demonstrated unlimited potential in wearable electronic devices other than energy storage like temperature alarm.

Deng et al [3] wrapping aligned carbon nanotube (CNT) onto shape memory polyurethane (SMP) substrate to develop a shape memory fiber shaped supercapacitor (SFSC). When SFSC deformed under bending and stretching and exceeds the thermal transition temperature, they restore their shape without affecting their electrochemical performances.

Graphene fiber supercapacitor called RGO-GO-RGO fiber was designed and fabricated by Hu et
During their development process they used laser irradiation of graphene oxide fiber (GO) to obtain a specific reduction graphene oxide fiber (RGO). In a single layer of graphene fiber RGO is integrated as electrode and GO as separator. This all in one graphene fiber has improved mechanical flexibility, lightweight and high performance so that it can be woven into textile for wearable electronics.

Graphene has high thermal conductivity and molybdenum disulfide (inorganic compound of molybdenum and sulfur) has high electrochemical conductivity. Wang et al [5] intercalated graphene sheets and molybdenum disulfide sheets which provide a large ion accessible surface area results in increase of excessive specific capacitance of 368 F/cm³.

Yang et al [6] stacked chemically converted graphene (CCG) sheets face to face. During their study they find out that water can serve as an effective spacer between the CCG sheets and prevent CCG restacking. If we talk about the macroscopic level CCG sheets, these are available in Self-stacked solvated graphene (SSG) film form, whose energy density, power density and operation rate is enhanced as compared to CCG.

First time Gopalsamy et al [7] prepared a metal oxide graphene fiber (Bi₂O₃ NT-graphene fiber) by a wet spinning process. This hybrid fiber supercapacitor has a stable cycling life of about 1000 cycles and this is compact in size thus reduce the space requirement as compared to other type of composites supercapacitor.

Woven cotton and polyester fabrics are widely used in textile industries now a days. Screen printing technique was used by Jost et al [8] to impregnate the porous carbon materials into woven cotton and polyester fabric. They also examined the porous carbon materials behaviour by using various other techniques such as cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy. Cotton and polyester based carbon electrodes are light in weight and have small electric resistance.

Wire shaped supercapacitor (WSS) gain much attention among researchers. Among various fiber electrodes carbon nanotube (CNT) fiber is the one which is light in weight, chemically inert and have high thermal and electrical conductivity. Xu et al [9] used spandex fiber as substrate and polyvinyl alcohol (H₂SO₄) gel as electrolyte and separator to produce a highly elastic and stretchable carbon nanotube fiber.

As per the necessity to fabricate that kind of supercapacitors which can sustain high tensile strains along with high capacitance performance Wang et al [10] developed a ultra-stretchable wire shaped supercapacitor to sustain tensile strain up to 850%. For this purpose two flexible carbon nanotube graphene manganese oxide fibers are helically wound around a super elastic core fiber.

Le et al [11] mainly worked in field of coaxial supercapacitor. They designed a Carbon microfibers (CMFs) coaxial supercapacitor with the help of multi-walled carbon nanotubes which are bundled as a core electrode and carbon nanofiber paper which is used as an outer electrode. This coaxial supercapacitor uses both type of carbon fibers micro and nano.

Graphene fiber based supercapacitors have limited electrochemical performance due to its serious stacking and hydrophobicity in aqueous medium. Chen et al [12] dispersed hydrophilic polyvinyl alcohol into a non-liquid crystalline graphene oxide and after that they used wet spinning and chemical reduction process for the development of a hybrid fiber. Their research work resulted a higher toughness, capacitance and hydrophilicity poly vinyl alcohol (PVA) or graphene hybrid fiber.

According to Liu et al [13] the electrode structure also affect the performance of fiber based supercapacitor. Mn₂O₃ cubic arrays on carbon fiber structure have been fabricated into straight, bent and coiled fibers supercapacitors among which coiled fibers supercapacitors showed excellent cyclic life time and higher capacitance.

A traditional hydrothermal method was used by Gu et al [14] to grow CuCo₂O₄ nano wire arrays on Ni wires. As compared to solid state fiber supercapacitors the energy and power density of these supercapacitors is higher.
The energy density of Fiber based supercapacitors is very low in comparison to conventional batteries. To overcome this drawback in energy density and to achieve superior electrochemical performances Li et al. [15] started their work for the development of a fiber shaped asymmetric supercapacitor (also called FASC). They used CNT-ZnO-NWs-MnO2 fibers as positive electrode and carbon nano tube fibers as negative electrode for the fabrication of FASC fibers. It has been judged that over 1000 bending cycles FASCs retained 96.7% of initial capacitance.

First time Senthilkumar et al. [16] used copper hexacyanoferrate coated carbon fibers (CuHCF@CFs) as the positive electrode and banana peel derived porous carbon coated carbon fibers (PC@CFs) as the negative electrode for the development of hybrid fiber supercapacitor (HFSC). Improved specific capacitance of 19.2 F g⁻¹ and energy density of 10.6 W h kg⁻¹ made these fibers to be suitable for wearable electronic devices.

Due to their tiny size and flexibility yarn supercapacitors reflect a great potential in textile for wearable electronics. Yarn supercapacitors have low energy density and since naked fibers are used for the fabrication of yarn supercapacitors (YSC) there may be short circuit when they come close to each other. A coaxial wet spinning assembly approach was proposed by Kou et al. [17] to prepare polyelectrolyte wrapped graphene/carbon nanotube/their mixture core-sheath fibers. The prepared YSCs have high energy density and no short circuit problem.

A lot of research work has been done in the fields of flexible electrodes (FEs) and flexible supercapacitors (FSCs). Dong et al. [19] divided FEs/FSCs into three main categories: fiber-like FEs/FSCs, paper-like FEs/FSCs and 3-D porous SCs and their corresponding FSCs. Fiber-like FEs/FSCs were subdivided into categories: plastic fiber supported FEs/FSCs, metal fiber supported FEs/FSCs, CF bundle supported FEs/FSCs, natural fiber supported FEs/FSCs, CNT yarn supported FEs/FSCs, GN fiber supported FEs/FSCs and electrochemically active fibers supported FEs/FSCs. Paper-like FEs/FSCs were subdivided into categories: freestanding paper-like FEs and flexible substrate supported paper-like FEs. 3-D porous SCs and their corresponding FSCs subdivided into categories: textile FEs/FSCs and sponge-like FEs/FSCs.

Dai et al. [19] worked for the development of a flexible solid state micro supercapacitor, to which they named pen-ink-carbon-fiber (Ink-CF). Their team simply coated the surface of carbon fibers (CFs) with ink. The developed Ink-CFs exhibit improved electrochemical performances such as at 5µA current, their specific capacitance is 4.31 mF cm⁻² and power density of 3.8x10⁻⁷ Wh cm⁻².

Electrodeposition method is used by Noh et al. [20] to directly grow the metal oxides of MnO2 and MoO3 on flexible carbon fibers (CFs). For the development of a high performance asymmetric supercapacitor (ASC), they assembled CF/MnO2 as positive electrode and CF/MoO3 as negative electrode. The fabricated ASC has high energy density of 2.70-1.78 µWh cm⁻² and a power density of 0.53-8.30 mW cm⁻².

To achieve a high energy density of 2 mWh cm⁻³ and power density of 11 W cm⁻³ under a high operating voltage of 1.6 V, Jin et al. [21] developed a fiber shaped asymmetric supercapacitor (FASC). These fibers have an advantage that their capacitance does not affect much when they embedded in a glove. For the fabrication of such fibers, Polyaniline (PANI) coated carbon fiber thread (PANI@CFT) is used as positive electrode and functionalized carbon fiber thread (FCFT) is used as negative electrode. FASC fibers have an advantage that even after stretching 100%, they maintain the same capacitance.

Urethane elastic fiber core spun yarns (UY) was used by Sun et al. [22] in a two-step process of carbon nanotubes (CNTs) dipping and polypyrrole (PPy) electrodeposition for the fabrication of a highly stretchable yarn supercapacitor. The obtained yarn supercapacitor is able to sustain a high capacitance of 69 mF cm⁻² under strain rate of 80%.

Considering working mechanism and electrode material (carbon/metal oxide/conductive polymer), Xue et al. [23] reviewed the recent achievements in flexible and wearable supercapacitors, especially in the area of yarn/fiber shaped and planer supercapacitors.
They also discussed the design of 1D yarn/fiber shaped flexible electrodes and 2D flexible electrodes.

Liu et al [24] fabricated a flexible wire-shaped fiber asymmetric supercapacitor (WFASC). They simply used MnO$_2$-PPy-carbon fiber composite as positive electrode and V2O5-PANI-carbon fiber composite as negative electrode for the fabrication of WFASC. It has been examined that V2O5 and MnO$_2$ has a work function difference with a large potential of 2.0 V. These supercapacitors exhibit a high aerial capacitance of 0.613 F cm$^{-2}$ and show a maximum energy density of 0.340 mWh cm$^{-2}$. Their power density is of the order of 30 mW cm$^{-2}$.

Pu et al [25] proposed a self-charging power textile with triboelectric nano-generator (TENG) fabric to harvest energy of human motion and yarn supercapacitor to store human motion energy which were integrated in a simple cloth. To achieve the high specific capacitance of 72.1 mF cm$^{-2}$, energy density of 1.6 mWh cm$^{-2}$ and power density of 2.42 mW cm$^{-2}$ with a capacitance retention of 96% in 10000 cycles, a common fabric yarn is need to be converted into highly conductive yarn, for which electrolysis deposition of Ni coating is followed by reduced graphene oxide (rGO) fibers coating.

Liu et al [26] worked in the area of enhancement of energy density and power density of 1D flexible supercapacitor, for which they developed a yarn supercapacitor. They integrated graphene-metallic textile composite electrode with low cost graphene sheets immobilized on the surface of Ni coated cotton yarns as current collector. In addition they used electrolysis process to deposit the Graphene on the surface of Ni cotton yarns.

To fulfill the need of a high performance electrode for redox supercapacitors, Lee et al [27] used Gradient biscrolling technique. For the fast transportation of ions they used biscrolling technique, where hundreds of layers of conducting polymer carbon nanotubes sheets (CNTs) are scrolled into 20 μm diameter yarn. To investigate the electrochemical performance of the scrolled yarn, electrodes in solid and liquid electrolyte two identical prepared electrodes were used.

Lu et al [28] used electrodeposition method to develop a high performance fiber based supercapacitor for wearable supercapacitors. To develop a hybrid carbon nanotube (CNT)/graphene/polyaniline (PANI) fiber, electrodeposition method is used, in which CNT/graphene fiber which was further coated with polyvinyl alcohol (PVA) phosphoric acid during wet spun process. The obtained hybrid fiber exhibit excellent elastic strain of 800%.

2. CONCLUSION:

After made review of the previous work undertaken in the fields of fiber based supercapacitors, it has been shown that these supercapacitors have many advances in terms of high capacitance, high energy density, long cycle life and easy to fabricate into woven to be used in wearable electronics. Carbon nano-tube based supercapacitors gain much popularity among researchers. To increase the utility and to achieve the remaining challenges a lot of works need to be done in future.

REFERENCES

1) Zhou Q, Jia C, Ye X, Tang Z and Wan Z (2016). A knittable fiber-shaped supercapacitor based on natural cotton thread for wearable electronics. *Journal of Power Sources* 327:365-373.

2) Huang Y, Zhu M, Pei Z, Xue Q, Huang Y and Zhi C (2016). A shape memory supercapacitor and its application in smart energy storage textile. *Journal of Materials Chemistry A* 4:1290-1297.

3) Deng J, Zhang Y, Zhao Y, Chen P, Cheng X and Peng H. A shape memory supercapacitor fiber. *Angewandte Chemie* https://doi.org/10.1002/anie.201508293.

4) Hu Y, Cheng H, Zhao F, Chen N, Jiang L, Feng Z and Qu L (2014). All-in-one graphene
based supercapacitor. *Nanoscale* **6** (2014) 6448-6451.

5) Wang B, Wu Q, Sun H, Zhang J, Ren J, Luo Y, Wang M and Peng H (2017). An intercalated graphene/ (molybdenum disulfide) hybrid fiber for capacitive energy storage. *Journal of Materials Chemistry A* **5** (2017) 9525-930.

6) Yang X, Zhu J, Qiu L and Li D (2011). Bioinspired effective prevention of restacking in multilayered graphene films: towards the next generation of high-performance supercapacitors. *Advanced Materials* **23** (2011) 2833-2838.

7) Gopalsamy K, Xu Z, Zheng B, Huang T, Kou L, Zhao X and Gao C (2014). Bismuth oxide nanotube graphene fiber based flexible supercapacitors. *Nanoscale* **6** 8595-8600.

8) Jost K, Perez CR, McDonough JK, Presser V, Heon M, Dion G and Gogotsi Y (2011). Carbon coated textile for flexible energy storage. *Energy and Environmental Science* **4** (2011) 5060-5067.

9) Xu P, Gu T, Cao Z, Wei B, Yu J, Li F, Byun J H, Lu W, Li Q and Chou T W. Carbon nanotube fiber based stretchable wire-shaped supercapacitors. *Advanced Energy Materials* https://doi.org/10.1002/aenm.201300759.

10) Wang H, Wang C, Jian M, Wang Q, Xia K, Yin Z, Zhang M, Liang X and Zhang Y (2018). Superelastic wire-shaped supercapacitor sustaining 850% tensile strain based on carbon nanotube graphene fiber. *Nano Research* **11** (2018) 2347-2356.

11) Le V T, Kim H, Ghosh A, Kim J, Chang J, Vu Q, A Pham D T, Lee J H, Kim S W and Lee Y H (2013). Coaxial fiber supercapacitor using all carbon material electrodes. *ACS Nano* **7** (2013) 5940-5947.

12) Chen S, Ma W, Xiang H, Cheng Y, Yang S, Weng W and Zhu M (2016). Conductive, tough, hydrophilic poly (vinyl alcohol)/graphene hybrid fibers for wearable supercapacitors. *Journal of Power Sources* **319** (2016) 271-280.

13) Liu B, Liu B, Wang X, Chen D, Fan Z and Shen G (2014). Constructing optimized wire electrodes for fiber supercapacitors. *Nano Energy* **10** (2014) 99-107.

14) Gu S, Lou Z, Ma X and Shen G. CuCo2O4 nanowires grown on a Ni wire for high performance flexible fiber supercapacitors. *ChemElectroChem* https://doi.org/10.1002/celc.201500020.

15) Li Y, Yan X, Zheng X, Si H, Li J, Liu Y, Sun Y, Jiang Y and Zhang Y (2016). Fiber-shaped asymmetric supercapacitors with ultrahigh energy density for flexible/wearable energy storage. *Journal of Materials Chemistry A* **4** (2016) 17704-17711.

16) Senthilkumar ST, Kim J, Wang Y, Huang H and Kim Y (2016). Flexible and wearable fiber shaped high voltage supercapacitors based on copper hexacyanoferrate and porous carbon coated carbon fiber electrodes. *Journal of Materials Chemistry A* **4** (2016) 4934-4940.

17) Kou L, Huang T, Zheng B, Han Y, Zhao X, Gopalsamy K, Sun H and Gao C (2014). Coaxial wet spun yarn supercapacitors for high-energy density and safe wearable electronics. *Nature Communications* **5** (2014) 3755.

18) Dong L, Xu C, Li Y, Huang Z H, Kang F, Yang Q H and Zhao X (2016). Flexible electrodes and supercapacitors for wearable energy storage: a review by category. *Journal of Material Chemistry A* **4** (2016) 4659-4685.

19) Dai S, Guo H, Wang M, Liu J, Wang G, Hu C and Xi Y (2014). Flexible micro-supercapacitortbased onpenink-carbonfiberthread. *Journal of Materials Chemistry A* **2** (2014) 19665-19669.

20) Noh J, Yoon CM, Kim YK and Jang J (2017). High performance asymmetric supercapacitor twisted from carbon fiber/MnO2 and carbon fiber/MoO3. *Carbon* **116** (2017) 470-478.

21) Jin H, Zhou L, Mak C L, Huang H, Tang WM and Chan HLW (2015). High performance fiber-shaped supercapacitors using carbon fiber thread (CFT) @polyaniline and functionalized CFT electrodes for wearable/stretchable electronics. *Nano Energy* **116** (2015) 662-670.

22) Sun J, Huang Y, Fu C, Wang Z, Huang Y, Zhu M, Zhi C and Hu H (2016). High performance stretchable yarn supercapacitor based on PPy@CNT@urethane elastic fiber core spun yarn. *Nano Energy* **27** (2016) 230-237.

23) Xue Q, Sun J, Huang Y, Zhu M, Pei Z, Li H, Wang Y, Li N, Zhang H and Zhi C. Recent progress on flexible and wearable supercapacitors. *Advanced Science News* https://doi.org/10.1002/smll.201701827.
24) Liu W, Liu N, Shi Y, Chen Y, Yang C, Tao J, Wang S, Wang Y, Su J, Li L and Gao Y (2015). Wireshaped flexible asymmetric supercapacitor based on carbon fiber coated with metal oxide and polymer. *Journal of Materials Chemistry A*, 3, 13461-13467.

25) Pu X, Li L, Li M, Jiang C, Du C, Zhao Z, Hu W and Wang ZL. Wearable self-charging power textile based on flexible yarn supercapacitors and fabric nanogenerators. *Advanced Materials*, https://doi.org/10.1002/adma.201504403.

26) Liu L, Yu Y, Yan C, Lia K and Zheng Z (2015). Wearable energy-dense and power-dense supercapacitor yarns enabled by graphene-metallic textile composite electrodes. *Nature Communications*, 6, 7260.

27) Lee JA, Shin MK, Kim SH, Cho HU, Spinks GM, Wallace GG, Lima MD, Lepro X, Kozlov ME, Baughman RH and Kim SJ (2013). Ultrafast charge and discharge biscrolled yarn supercapacitors for textiles and micro devices. *Nature Communications*, 4, 1970.

28) Lu Z, Foroughi J, Wang C, Long H and Wallace GG. Superelastic hybrid CNT/graphene fibers for wearable energy storage. *Advanced Energy Materials*, https://doi.org/10.1002/aenm.201702020.