Flexible Supercapacitors: A Materials Perspective

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Flexible supercapacitors are highly attractive for the large number of emerging portable lightweight consumer devices. The novelty of a flexible supercapacitor is the incorporation of flexible electrode or substrate material to combine structural flexibility with the inherently high power density of supercapacitors. Flexible supercapacitors can use non-Faradaic energy storage process as seen in the electric double layer capacitor type or a Faradaic mechanism as seen in the pseudocapacitors (PCs). In this review, we account the current progress in pseudocapacitive electrode materials, fabrication techniques and new materials for electric double layer capacitor, and different flexible substrates. Future directions in developing new materials toward improved energy density and cost-effectiveness of the flexible supercapacitors and their usage in combination with lithium-ion batteries are highlighted.

Keywords: flexible supercapacitor, electrode materials, oxides, chalcogenides, molybdates, flexible substrates

INTRODUCTION

Flexible energy storage devices are fundamental to the development of next-generation wearable, compact, and portable electronics for medical, military, and civilian applications e.g., flexible displays on phones, health tracking devices, computers, and televisions (Ko et al., 2017). To this end, flexible supercapacitors are highly attractive in comparison to batteries (LIBs) as they combine the inherent high power density (> 10 kW/kg), fast charging/discharging capability, longer operation lifetime, and mechanical flexibility. Conventional supercapacitors consist of an outer case, current collectors in the form of metal foils, and positive and negative electrodes in electrolyte separated by ion transport layer. In flexible supercapacitors, the highly conducting and flexible carbon network serve as both the electrode and current collector. A schematic and an example of a flexible supercapacitor is shown in Figure 1. Therefore, the structural architecture of flexible supercapacitors is made lightweight and further simplified for portable electronics. Another key difference from conventional supercapacitors is that each component in flexible supercapacitors (e.g., electrodes and packing shell) is flexible. These flexible supercapacitors can typically be of two types, electric double-layer capacitors (EDLCs), and pseudocapacitors (PCs) (Chee et al., 2016; Liu et al., 2017). EDLCs use the non-Faradaic electrostatic process to store energy. They function based on the charges accumulated at the interface between the electrolyte and the electrode, which is primarily carbon-based materials with the high specific area. In PCs, the electrode formed from conductive polymers or metal oxides use a Faradaic mechanism to store charges.

A combination of indices e.g., energy and power density, cycling stability, and areal capacitance (capacitance per unit area, Fcm⁻²) determine the performance of a flexible supercapacitor. The following section highlights the equations used to assess performance metric of EDLC and PC flexible supercapacitors.
Electric Double-Layer Capacitors

In EDLCs, the charge accumulated at the electrode/electrolyte interfaces or capacitance $C$ can be found using Equation 1 (Endo et al., 2001).

$$C = \frac{\varepsilon}{4\pi\delta} \int dS$$

where, $\varepsilon$ is the dielectric constant of the electrolyte, $S$ is the electrode interface surface area, and $\delta$ is the distance from the center of the ion to the electrolyte interface. In recent literature, the specific capacitance has been calculated from the area under the cyclic voltammetry (CV) curve using Equation 2 (Kim et al., 2014).

$$C = k \int \frac{i}{mS}$$

where, $i$ is the integrated area of the CV curve, $m$ is the mass of the electrode material, $S$ is the scan rate of the CV conducted, and $k$ is a constant multiplier. The specific capacitance can also be obtained from galvanostatic discharge profile following Equation 3 (Wang et al., 2014; Zhou et al., 2014).

$$C = k \int \frac{it}{\Delta Vm}$$

where, $i$ is the current, $t$ is the time elapsed during the discharge process, $m$ is mass of the electrode material, and $V$ is the working potential range.

Finally, the energy density ($E$) and power density ($P$) for EDLCs are calculated from the CV profile, following Equations 4 and 5, respectively (Winter and Brodd, 2004; Fan et al., 2011).

$$E_{cell} \left( \frac{Wh}{kg} \right) = \frac{1}{2}CV^2$$

$$P_{cell} \left( \frac{W}{kg} \right) = \frac{E_{cell}}{\Delta t}$$

where, $\Delta t$ is the discharge time.

Pseudocapacitors

Recently, the following method has been used to determine the performance parameters for a PC flexible supercapacitor. The stored electrode charge, $q$ for PCs is calculated from the mass of PC material ($m$), the specific capacitance ($C$), and the range of CV operation ($\Delta E$) following Faraday’s law (Equation 6) (Khomenko et al., 2006).

$$q = C \times \Delta E \times m$$

The electrochemical capacitances for CV and galvanostatic charge/discharge measurements in this type of supercapacitor are determined using Equations 7 and 8, respectively (Zhang and Pan, 2015).

$$C = \int \frac{i(V)}{2\Delta VS}$$

$$C = \frac{I \Delta t}{\Delta V}$$
where, \( i, v, I, \) and \( S \) are attributed to current, scan rate (mVs\(^{-1}\)), applied current density, and active electrode area, respectively. The two major performance indices \( P \) and \( E \) are calculated from the galvanostatic discharge profile following Equations 9 and 4, respectively for PCs (Khomenko et al., 2006).

\[
P = \frac{V^2}{4RS} \tag{9}
\]

where, \( R \) is the total resistance found using the voltage drop between two points in the discharge profile (\( \Delta IR \)) and the applied current (\( i \)) as follows (Equation 10) (Khomenko et al., 2006; Zhang and Pan, 2015):

\[
R = \frac{\Delta IR}{2i} \tag{10}
\]

Therefore, power and energy densities are two defining parameters for the performance of a flexible supercapacitor, in combination with its structural flexibility. Supercapacitors are prized for their high power density. Though the energy density (\( \sim 5 \text{ Whkg}^{-1} \)) of supercapacitors is lower as compared to LIBs (\( \sim 150 \text{ Whkg}^{-1} \)), there has been enormous advancements in nanostructured materials for supercapacitor electrodes and functional electrolytes to improve the energy density. The flexible and conducting electrode that also serves as the current collector is a key component for flexible supercapacitors. Therefore, materials for the electrodes are being constantly improved (Li et al., 2016). Novel device fabrication techniques are also being pursued to achieve higher architectural flexibility at lower cost. Recently, Dong et al. reported three broad classifications of flexible supercapacitors into fiber-like, paper-like, and three-dimensional porous materials based on their microstructure and morphology in an attempt to summarize the huge advances in the field (Dong et al., 2016a). The structural design and its associated fabrication techniques also greatly influence the flexibility of supercapacitors as summarized in the review by Zhang et al. (2015). This brief review captures the recent advances made in electrode materials for flexible supercapacitors.

**RECENT PROGRESS IN FLEXIBLE SUPERCAPACITOR MATERIALS**

Recently, a wide range of new pseudocapacitive electrode materials has been investigated with the aim of increasing the energy density of flexible supercapacitors. PCs essentially have a higher charge storage capacity compared to the EDLCs but are limited by high cost and poor cyclic stability. Nanostructured redox active materials are attractive for PCs as they can increase the active sites for Faradaic redox reaction at the electrode/electrolyte interface for enhanced charge storage. To this end, a large group of transition metal oxides are known for their promising pseudocapacitive behavior. Conventionally, several binary metal oxides (e.g., iron oxide, RuO\(_2\), NiO, CoO\(_2\)O\(_4\), MoO\(_2\)O\(_3\), V\(_2\)O\(_5\), and MnO\(_2\)) have exhibited large energy and power density. Among them, RuO\(_2\) in its hydrous form has been known to surpass the capacitance of carbon-based and conducting polymeric materials (Hu and Chen, 2004; Oh and Nazar, 2010). MnO\(_2\) has also proved to be promising for its environmental benignity, cost-effectiveness, and good specific capacitance (Lee and Goodenough, 1999; Hu and Chen, 2004; Miller and Simon, 2008). However, ternary and higher order metal oxides are specifically attractive because they provide additional sites for pseudocapacitive redox processes to facilitate higher capacitance. For example, the ternary oxide NiCo\(_2\)O\(_4\) is highly suitable for supporting multiple electrochemical processes as it contains mixed valence metals (Zhang and Lou, 2013; Zhang D. et al., 2014). NiCo\(_2\)O\(_4\) nanocrystals grown on different substrates such as carbon fiber paper, nickel foam, and titanium sheets have shown good cyclic stability and high capacitance (Zhang et al., 2012; Huang et al., 2013; Mitchell et al., 2015). Recently, a highly flexible quasi solid-state supercapacitor device was fabricated by sandwiching electrodes of flower-shaped NiCo\(_2\)O\(_4\) nanocrystals on graphene oxide (GO) substrate (Gupta et al., 2015). The device showed excellent cyclic stability, suggesting that this NiCo\(_2\)O\(_4\)-GO electrode material is highly suitable for fabrication of variable temperature and high performance flexible supercapacitor devices.

Transition metal chalcogenides (VS\(_2\), CuS, CoE\(_2\), NiE\(_2\), E = S, Se), rare-earth metal sulfides (LaS\(_3\) and SmS\(_2\)), and layer-structured chalcogenides (MoS\(_2\) and SnSe) form another class of attractive electrode material for flexible supercapacitors because of their chemically rich surface area to host redox reactions (Feng et al., 2011; Cao et al., 2013; Ratha and Rout, 2013; Jiang et al., 2014; Peng et al., 2014; Wei et al., 2014; Zhang C. et al., 2014). Ternary and higher-order chalcogenide-based materials have recently been successfully synthesized owing to tremendous advances in wet-chemical synthesis techniques (Ramasamy et al., 2014b, 2015). These materials are further appealing for supercapacitor electrodes as they contain different metal ions to facilitate rich redox reactions and the tunable gap between the layers can host a wide range of ions from the electrolyte to enhance the specific capacitance. For example, the CuSbS\(_2\) and CuSbSe\(_2\)-x mesocrystals provided exceptional cyclic stability at high current densities, making them attractive for fast charging applications (Ramasamy et al., 2014a,c).

There have been several works on metal molybdate hetero-structures as they are cost-effective, environment-friendly, and show high electrochemical performance. Different morphologies and composition of molybdates e.g., three-dimensional MnMoO\(_4\)/CoMoO\(_4\) hetero-structures, CoMoO\(_4\)-graphene composite, hierarchical NiMoO\(_4\) nanospheres, and NiMoO\(_4\) nanowires have been investigated (Mai et al., 2011; Cai et al., 2013; Xia X. et al., 2013). In NiMoO\(_4\), it was observed that the spherical morphology facilitated increased capacitance owing to its high surface area and electrical conductivity. The effect of morphology was investigated in detail with shape-controlled CoMoO\(_4\) nanostructures (e.g., cauliflower, brick-like, and spherical) (Candler et al., 2015). The charge storage capacity of the material is dependent on its morphology. The flexible supercapacitor device fabricated with the shape-controlled cobalt molybdate electrodes exhibited improved stability with an increase in number of cyclic CV performance. The device was also found to be an attractive candidate for high-temperature...
supercapacitor operations. Figure 2 shows the new ternary metal oxide, higher order chalcogenide, and metal molybdate pseudocapacitive electrode materials synthesized.

In a recent breakthrough, Ko et al. reported a new ligand-mediated layer-by-layer technique to assemble metal (Au) and metal oxide (MnO) pseudocapacitive nanoparticles on flexible paper substrate to form supercapacitor electrodes (Ko et al., 2017). The device showed substantially high energy (15.1 mWcm⁻²) and power (267.3 µWcm⁻²) densities. The method is an improvement over conventional physical adsorption processes like dip coating, painting, Meyer rod coating, and dispensing-writing because it allows controlled loading of both the conducting polymer and the active materials onto the substrate. In another breakthrough report, a lamellar electrode material of vanadium nitride nanodots intercalated in carbon nanosheets has shown an ultrahigh volumetric capacitance (1203.6 F cm⁻³ at 1.1 A cm⁻²; rate capability of 703.1 F cm⁻³ at 210 A cm⁻²) that exceeds most carbon-transition metal oxide/nitride PCs known to date (Gao et al., 2015; Li et al., 2018). This vanadium nitride based electrode is a significant improvement over previous reports of vanadium nitride nanostructures with limited specific surface area and capacitive performance. Therefore, the type of material and assembly technique are two key parameters to achieve high performing charge storage in flexible PCs. Liu et al. recently developed a new oxidative chemical vapor deposition method for fabricating electrodes coated with pseudocapacitive poly(3,4-ethylene dioxythiophene) polymer (Liu et al., 2017).

As seen from the literature review, one of the primary strategies to render the PCs flexible and lightweight for suitable operation has been to use a variety of cost-effective and eco-friendly flexible substrates (e.g., metals, carbon paper and foam, conventional paper, textile, sponge, and cable). Metal substrates have the merits of high electric conductivity and mechanical strength (Dubal and Holze, 2013a; Dubal et al., 2013; Jagadale et al., 2013). Flexible stainless steel has been one of the most widely used metal substrates to directly fabricate electroactive electrode materials such as MnO₂ nanorod forests and shape-controlled Ni(OH)₂ nanostructures (Gund et al., 2013; Santhanagopalan et al., 2013). Electrodeposition has been used to form Co(OH)₂ nanoflake films on flexible stainless steel substrates (Chou et al., 2008). Facile chemical methods have also been reported for depositing stacked Mn₃O₄ nanosheets, Mn₃O₄ thin films, as well as nanostructured polyaniline electrode materials on flexible stainless steel substrates (Dhawale et al., 2011; Dubal et al., 2012; Dubal and Holze, 2013b). These stainless steel supercapacitors are highly promising in terms of long-term stability. Other metallic substrates, including Al, Ti, Cu, and Ni-foam, have also been successfully used to fabricate hierarchical and bendable supercapacitors with excellent cycling stability (Liu et al., 2010; Le et al., 2011; Lin et al., 2011; Yuan et al., 2011; Zhang et al., 2011; Kai et al., 2012; Kim et al., 2012; Wang et al., 2012, 2013; Zhou et al., 2012, 2013; Dorfler et al., 2013; Reit et al., 2013; Xia H. et al., 2013). Metal-supported flexible electrodes are however, opaque and less stretchable. Therefore, flexible plastic substrates are preferred in supercapacitor electrodes for touch-screen displays (Yu et al., 2010; Niu et al., 2013; Shi et al., 2013a; Chen et al., 2014; Hao et al., 2014). Flexible supercapacitor electrodes of graphene films supported on polyethylene terephthalate (PET), MnO₂ nanosheets on indium tin oxide-PET substrates, or single-walled carbon nanotubes on polydimethyldioxane and polyaniline substrates have proved to be highly promising for transparent electronics in terms of capacitance and stretchability. However, plastic substrates
are limited in electrical conductivity. Paper-based flexible supercapacitors, being lightweight, bendable, transparent, and easily processable are attractive alternatives for electronic screens of portable devices (e.g., mobile phones, digital cameras, and laptops). In this regard, both free-standing electrodes such as carbon nanotube (CNT)-paper composites and deposition of PCs on recyclable paper substrates have been successfully investigated. The hierarchical macroporous and network-free morphology in flexible sponge substrates facilitate high liquid absorption, increased surface area, continuous coating, and enhanced interaction between electrodes and electrolyte. Symmetrical flexible supercapacitors consisting of CNT sponge assembly and synthesized via chemical vapor deposition have been reported to show excellent cyclic stability (Li et al., 2013). In addition, Fe$_3$O$_4$ and MnO$_2$ are attractive PC materials to further increase the energy density of carbonaceous sponge substrates (Chen et al., 2011; Wu et al., 2013). Textile substrates like cotton cloth, polyester microfiber twill, and carbon fabric are synthesized from natural or synthetic fibers via weaving, pressing, knitting, or felting. These substrates have the advantage of high stretchability, lightweight, three-dimensional open-pore structure, good mechanical strength, and low cost compared to other substrates for flexible supercapacitors. Stretchable textile electrodes have been fabricated by impregnating single-walled carbon nanotubes into cotton cloth or porous carbon materials into woven cotton/polyester textile (Hu et al., 2010; Jost et al., 2011). To further increase the electrochemical capacitance, metal oxide nanoparticles (e.g., MnO$_2$) have been coated on carbon fiber-based textile substrates to form the flexible electrodes (Yuan et al., 2012; Zhao et al., 2013; Tao et al., 2014; Yang et al., 2014a,b). The electrochemically active material coating is the primary contributor for the total capacitance of textile-based flexible electrode, since textiles have inherently low capacitance. Therefore, a flexible activated carbon felt/MnO$_2$/CNT assembly have recently been fabricated to obtain enhanced capacitance and high performance (Dong et al., 2016b). In addition, metal-organic frameworks (MOFs), a class of co-ordination polymers having high specific surface area and controllable pore size to anchor the active materials are being used to address the limitations of carbon textile substrates (Xu et al., 2017; Liu et al., 2018; Zhao et al., 2018). The MOFs can be applied in three ways for flexible supercapacitors, directly as an electrode material, as a composite electrode, or as a flexible substrate for active electrode materials (Zhao et al., 2018). Polyoxometalates are another class of porous substrates with novel electronic properties, robust structure, and capability to behave like an acid during synthesis owing to their metal-oxygen clusters. The polyoxometalates have recently been used to significantly improve the electrical conductivity of low-cost electrode materials like MnO$_2$ nanoparticles (Wang et al., 2018). Another emerging direction in flexible substrates is biomass-derived substrates and wood substrates (Lv et al., 2015; Herou et al., 2018). Wood transverse section slice is a promising candidate for flexible substrates as it shows excellent hydrophilic property, but does not require any harsh and expensive chemical processing steps involved in the preparation of other substrates (e.g., cellulosic paper). Recently, a new anode material of low crystalline FeOOH nanoparticles coated on carbon fiber cloth has achieved both high energy (104 Wh kg$^{-1}$) and power (1.27 kW kg$^{-1}$) densities (Owusu et al., 2017).

EDLCs primarily use carbon materials as electrode (Hu et al., 2010; Dong et al., 2016a). The single carbon electrodes in EDLCs are made of carbon networks (e.g., carbon fabric, cloth, film, coating, paper, or textile) fabricated from one dimensional (1D) carbon nanotubes or carbon fibers and/or two dimensional (2D) graphene or graphite sheets (Weng et al., 2011; Chen and Dai, 2014). Different fabrication techniques like weaving, chemical vapor deposition, filtration, printing, evaporation, or dip-drying are used to form carbon networks by van der Waals interaction or hydrogen bonding of carbon particles (Cheng and Liu, 2013; Tan et al., 2017). Carbon fabric, a highly suitable carbon network for flexible supercapacitors in terms of strength, stiffness, and flexibility is primarily manufactured by plain, satin, or twill weaving technique (Cheng and Liu, 2013; Qian et al., 2013; Dong et al., 2016a). A stable dispersion of carbon material and ligand such as sodium dodecylbenzene sulfonate in a suitable solvent serves as the starting agent for the other types of carbon network including carbon film, paper, or textile. Carbon films can be formed using chemical vapor deposition to assemble single-walled carbon nanotubes on polydimethylsiloxane substrates. They can also be formed by ink-jet printing or spin-coating the carbon materials on flexible plastic or paper substrates. Paper forms a highly suitable substrate due to its high porosity and surface area, but large pore sizes can cause the carbon nanostructures to penetrate into the substrate (Lee et al., 2017) (Pushparaj et al., 2007). Applying polyvinylidene fluoride coating on the substrate has been used as a facile pre-treatment method to facilitate maximum adhesion of carbon electrode materials to the porous paper substrate while maintaining the electrical conductivity. Carbon paper, in contrast, is prepared by the filtration or evaporation techniques. A dipping-drying method similar to the cloth dyeing process is essentially used to fabricate carbon textiles. In a typical synthesis, the fabric is dipped in the pre-formed dye solution containing carbon materials before drying the solvent from the fabric to form the electrode. In addition to the electrode material, an ultrathin in-plane geometry of the electrode is seen to facilitate higher interaction of the electrode/electrolyte for EDLCs as compared to a planar stacked geometry (Chen and Dai, 2014). Vertical alignment of the active electrode material on the substrate has also been known to significantly enhance the capacitance (Izadi-Najafabadi et al., 2010; Eftekhar, 2018). Investigating the underlying mechanism of the role played by alignment in graphene supercapacitors will be a key future direction in increasing the energy density in EDLCs and building ultrastack supercapacitors (Eftekhar, 2018).

Recently, ionic liquids have been successfully investigated as solvent/electrolyte for EDLCs due to their attractive properties like high ionic conductivity, a wide range of electrochemical potential, and excellent moisture stability, and relatively low volatility (Lehtimaki et al., 2015; Lorenzo and Srinivasan, 2018). In addition to graphene and carbon based EDLCs, black phosphorus, a two-dimensional layered and p-type direct band-gap semiconducting electrode material has recently coupled high power density with high energy density in EDLCs (Yang et al., 2017).
CONCLUSION

In this review, we have summarized the recent progress in the development of novel electrode materials of high specific supercapacitance for both EDLC and PC flexible supercapacitors. Ternary and higher order nanostructures of metal oxides, layered structure transition metal chalcogenides, metal molybdates, vanadium nitride, and polylpyroxtetate-MnO$_2$ have proved attractive for PC electrodes. The shape-controlled CoMoO$_4$ nanostructure PC electrodes are promising in high-temperature operation. Advances in EDLC electrodes such as new fabrication techniques and use of ionic liquids as solvent/electrolytes have been described in the review. In addition, we have summarized the emerging advances in low-cost flexible substrates in terms of material categories (e.g., metal, paper, carbon-paper, sponges, textiles, or cable-type substrates) and their corresponding advantages and limitations.

In brief, flexible supercapacitors are highly attractive for their excellent power density and the major challenges in the technology lie in their low energy density and high production cost. Therefore, one of the future directions in flexible supercapacitors is combining commonly found EDLC materials with cost-effective PC active materials to form novel hybrid electrodes. Recently, a significant increase in energy density (104.3 Whkg$^{-1}$) has been achieved with a hybrid supercapacitor composed of a capacitive dominant anode of iron oxide hydroxide nanoparticles grown on flexible carbon fiber cloth and a PC NiMoO$_4$ cathode, while maintaining exceptional stability and power density (Owusu et al., 2017). Another scientific thrust is to develop solution-based processes and robust fabrication routes for large-scale manufacturing of flexible supercapacitors. Novel electrolytes and electrode materials are also being investigated to enable high-temperature operation of the flexible supercapacitors. Therefore, flexible supercapacitors is a rapidly advancing and environment-friendly technology for energy storage. It is envisioned to both serve as a primary energy storage and in combination with LIBs.

AUTHOR CONTRIBUTIONS

SP was responsible for writing and formatting the article. KR wrote and communicated the manuscript. RG and AG supervised and wrote the manuscript.

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Conflict of Interest Statement: KR is employed by UbiQD, Inc.
The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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