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Review

Flexible supercapacitors

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ABSTRACT

Flexible supercapacitors show a great potential for applications in wearable, miniaturized, portable, large-scale transparent and flexible consumer electronics due to their significant, inherent advantages, such as being flexible, lightweight, low cost and environmentally friendly in comparison with the current energy storage devices. In this report, recent progress on flexible supercapacitors, flexible electrodes and electrolytes is reviewed. In addition, the future challenges and opportunities are discussed.

Contents

1. Introduction

Energy has become an issue of national security for every country on earth. Meeting energy needs in an environmentally sustainable manner is currently the most important technological challenge facing society. Energy storage devices can efficiently store electricity generated from renewable sources, such as solar, water, wind, thermoelectric, fuel cells, for reuse at many different scales. Therefore, energy storage devices, such as batteries and supercapacitors, have become key to society (Guerrero, Romero, Barrero, Milanes, & Gonzalez, 2009; Liu, Li, Ma, & Cheng, 2010; Wang, Wei, & Qi, 2007). Electrochemical capacitors (supercapacitors) have been progressing rapidly in recent years. Because they have a particularly high power density, long life cycle, rapid charge/discharge, a wide operating temperature range, environmentally benign and safe (Wang et al., 2007; Zhang et al., 2009), supercapacitors show a great potential in both consumer electronics and large-sized energy storage applications, such as in the communications, transportation, aviation and power industries. Supercapacitors have been produced at an industry scale and commercialized for decades. Typically, a supercapacitor includes a plastic outer package, positive electrode, negative electrode, and separators. The electrodes, the key to a supercapacitor, are generally made from active powder materials, conductive additives and binders. The active material and conductive additive powders are brought together on a metal current collector by binders at several weight percents. Then, the positive and negative electrodes together with the separators are folded into several layers, either rectangular shaped or wired to be cylindrically shaped (Burke, 2000).

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Because the concept of wearable, miniaturized, portable, flexible electronic products is being put forward, there is currently a strong need for the development of new, flexible, lightweight, low-cost and environmentally friendly energy storage devices. However, the state-of-the-art supercapacitors are far from their potential. Therefore, particular attention is now being given to transparent and/or flexible supercapacitors. Large-scale transparent, flexible electronic devices have been pursued for their potential applications in touch sensors and display technologies (Hu, Zhu, Wang, & Chen, 2011; Ju et al., 2008; Nyholm, Nystrom, Mihranyan, & Stromme, 2011; Pushparaj et al., 2007; Wei et al., 2009). In this paper, the recent progress on flexible supercapacitors, flexible electrodes and electrolytes is reviewed. In addition, the future challenges and opportunities are discussed.

2. Flexible electrodes

Two types of supercapacitors are based on the charge storage mechanism: the electric double-layer capacitor (EDLC) and pseudocapacitor. Carbon materials are typically used as electrode materials of an EDLC, whereas pseudocapacitor materials include metal oxides and conducting polymers (Xu, Kang, Li, & Du, 2010; Xu, Wei, Li, Kang, & Guan, 2011).

Flexible electrodes are primarily based on carbon materials (Pushparaj et al., 2007; Wang et al., 2009). Carbon materials have a variety of geometric shapes from a macroscopic point of view, such as zero-dimensional (0D) fullerene or carbon particles, one-dimensional (1D) carbon nanotubes (CNTs) or carbon fibers (CFs), and two-dimensional (2D) graphene or graphite sheets (Fig. 1(a)). Among them, 1D and 2D carbon materials have been widely used in flexible electrodes because they can readily form highly conductive and flexible carbon networks (such as carbon fabric, carbon film, carbon paper and carbon textile, as shown in Fig. 1(b)) with outstanding electrochemical performances.

Based on these carbon networks, we can roughly divide flexible electrodes into two categories: single carbon electrodes and carbon composite (CC) electrodes. Single carbon electrodes are composed of only carbon networks made from one or more carbon shapes, whereas carbon composite electrodes are composites of versatile carbon networks with various pseudocapacitor materials.

2.1. Single carbon electrodes

Carbon networks consisting of carbon fabric, cloth, film, coating, paper or textiles are important in the development of flexible electrodes. These carbon architectures generally come from single 1D and/or 2D carbon particles, which form aggregates by hydrogen bonds or van der Waals forces (Hu & Cui, 2012; Hu, Pasta, et al., 2010; Hu, Wu, La Mantia, Yang, & Cui, 2010). Various methods have been used to create carbon networks from 1D or 2D carbon particles, such as weaving, chemical vapor deposition (CVD), printing, filtration, evaporation and dipping-drying (Fig. 1(b)). In this section, we explain the preparation procedures for carbon cloth, film, paper, and textiles.

The best-known network used for flexible electrodes is carbon fabric (CF), which can be fabricated by carbon fibers through a commercial weaving method (Fig. 1(b), F1). Carbon fabrics manufactured with a loom commonly use the three main weave styles: plain, satin and twill weaves (Fig. 2). In addition, fibers can be mixed to obtain hybrid fabrics. Woven fabric exhibits good strength, stiffness, and excellent flexibility; however, its low capacity severely

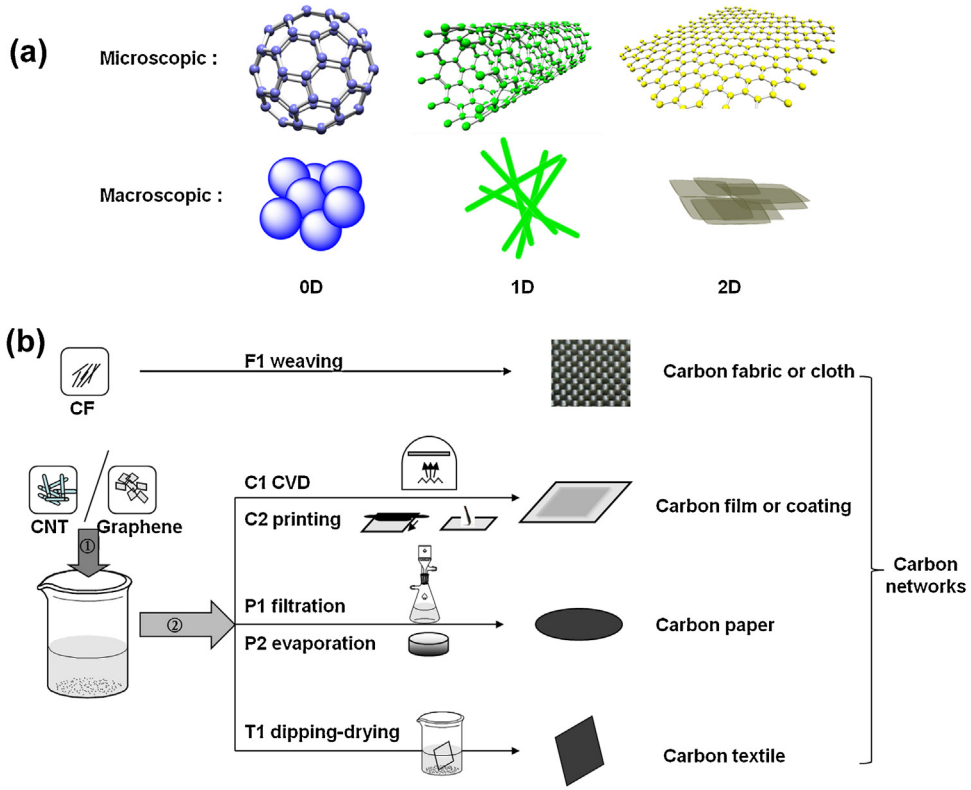

Fig. 1. (a) Schematic illustration of 0D, 1D, and 2D carbon materials at the microscopic and macroscopic scale. (b) Fabrication of carbon networks with 1D carbon fibers (CF), 1D carbon nanotubes (CNTs) or 2D graphene as the starting materials using a variety of methods. With carbon fibers as the raw material, carbon fabric or cloth is fabricated by weaving (F1); With CNTs or graphene as the raw material, carbon films or coatings are fabricated by CVD (C1) or printing technology (C2), carbon paper is synthesized using a filtration method (P1) or an evaporation process (P2), and carbon textile is prepared via a dipping-drying method (T1).

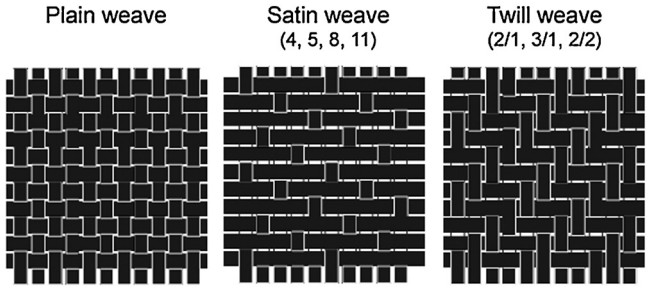

Fig. 2. Three weave styles of carbon fabrics. Adopted from Hexcel Corporation.

limits its application for electrodes (Masarapu, Wang, Li, & Wei, 2012). Therefore, woven fabric combined with pseudocapacitor materials are important in the following carbon composite electrodes (Reddy, Amitha, Jafri, & Ramaprabhu, 2008).

The other three carbon networks, which include carbon film, carbon paper, and carbon textile, are achieved by using 1D carbon nanotubes or 2D graphene sheets as the starting materials via a variety of methods. As described in Fig. 1, the procedure to create the three carbon networks all involve a similar starting procedure, which is the dispersion of carbon materials in a suitable solvent to produce a stable solution (also known as conductive ink in printing process and dye solution in dipping-drying technology). Importantly, surfactants, such as sodium dodecylbenzene sulfonate, are also necessary for good dispersion.

Carbon films are usually fabricated by a CVD method and a printing process (Fig. 1(b), C1 and C2). A buckled single-walled carbon nanotube (SWNT) film has been prepared with a simple CVD method on an elastomeric polydimethylsiloxane (PDMS) substrate followed by the relaxation of the prestrained substrate (Yu, Masarapu, Rong, Wei, & Jiang, 2009). The electrochemical performance of the supercapacitor assembled by SWNTs macrofilms is not influenced by the change in bending degree as shown in experiments performed at different levels of prestrain load on the substrate. We note that the printing process refers to printing of specially made inks on a substrate with Meyer rods, brushes (Fig. 1(b), C2), ink-jet printers or spin-coating tools (Chen, Chen, Qiu, & Zhou, 2010; Grande et al., 2012; Hu & Cui, 2012). The substrate can be flexible plastic or paper; paper has a relatively high conductivity due to its porous structure, which leads to a large contact area and good adhesion with inks. It has been found that the sheet resistance of printed paper by a scalable Meyer rod coating method is as low as 10 Ω/sq (Hu et al., 2009; Hu & Cui, 2012). However, occasionally, certain pores in the paper can be too large, which results in nanotubes penetrating into the pores, leading to the supercapacitor being short-circuited. To avoid this outcome, a surface pretreatment that applies coatings onto both faces with polyvinylidene fluoride (PVDF) has been applied (Kaempgen, Chan, Ma, Cui, & Gruner, 2009).

The preparation of carbon papers is represented in Fig. 1(b) (P1 and P2). Suspensions of 1D carbon materials can become free-standing paper after a filtration method (Kang, Li, Hou, Wen, & Su, 2012; Yu, Roes, Davies, & Chen, 2010) or an evaporation procedure (Izadi-Najafabadi et al., 2011; Torop et al., 2011). In the filtration process, special paper is fabricated by carbon materials through hydrogen bonds or van der Waals forces in the filter membrane. The carbon paper can be used as an electrode directly (Kang et al., 2012) or after a further treatment (Yu et al., 2010) to remove the filter membrane by transferring it onto a plastic substrate. For example, graphene/cellulose paper can be fabricated by filtrating the mixed solution of graphene sheets with cellulose pulp. Moreover, it has been shown that a supercapacitor assembled by two flakes of graphene/cellulose papers in an organic electrolyte of 1 M $LiPF_6$ in ethylene carbonate/propylene carbonate/dimethyl carbonate (EC/PC/DMC = 1:1:1) exhibited a large specific capacitance, approximately 252 F/g at a current density of 1 A/g (Kang et al., 2012). In addition, self-standing carbon paper can be created by evaporating solvent on a Petri dish (Izadi-Najafabadi et al., 2011) or a special mold (Pushparaj et al., 2007; Torop et al., 2011). These paper-making methods are also extensively used in fabricating carbon composite electrodes, which will be further described subsequently.

Carbon textiles are fabricated by dipping-drying technology, which is similar to the cloth dyeing process in the cloth industry. As the T1 procedure is described in Fig. 1(b), a piece of fabric is dipped into a pre-made solution (so-called dye solution), and then, the solvent is removed after drying (Hu, Pasta, et al., 2010; Pasta, La Mantia, Hu, Deshazer, & Cui, 2010). Used as electrodes, these highly conductive carbon textiles have outstanding flexibility and exhibit outstanding electrochemical performance. Mauro Pasta et al. (2010) fabricated a SWNTs textile by this method with a sheet resistance as low as 1 Ω/sq and demonstrated that aqueous supercapacitors made from these textiles in a Li_2SO_4 electrolyte displayed a specific capacitance of 70–80 F/g at a current density of 0.1 A/g, which rarely decreased after 35,000 cycles. Hu and Cui (2012) concluded that coating pseudocapacitor materials (such as MnO_2) onto these textiles can greatly increase their specific capacitance.In addition to the methods listed in Fig. 1(b), Zheng, Hu, Wu, Xie, and Cui (2011) fabricated flexible electrodes through a solvent-free drawing method, which can directly draw a graphite rod onto cellulose paper. By using 1 M H_2SO_4 as the electrolytes, the supercapacitor exhibits a capacitance of 23 F/g at a current density of 0.2 A/g. El-Kady, Strong, Dubin, and Kaner (2012) reported that a flexible graphene-based electrode (graphene films) can be produced by low-power infrared laser reduction of graphite oxide films with a standard Light Scribe DVD optical drive. The specific capacitance of such an electrode has reached 265 F/g in tetraethylammonium tetrafluoroborate dissolved in acetonitrile and 276 F/g in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate.

2.2. Carbon composite electrodes

EDLC materials are known to store energy according to the electric double-layer effect at the electrode/electrolyte interface. However, the specific capacitance values of single carbon electrodes are small. Hence, pseudocapacitive materials, which involve a fast and highly reversible redox reaction for charge storage, have been coated onto the carbon infrastructure to increase the specific capacitance of flexible electrodes.

In recent years, much effort has been devoted to coating various metal oxides or polymer materials onto carbon networks by solution-based methods (Fig. 3). Metal oxides are coated onto carbon networks through electrodeposition (Bao & Li, 2012; Chen et al., 2011; Hu, Chen, et al., 2011; Kang, Kim, Chung, & Kim, 2010; Lu et al., 2012; Yu et al., 2011; Yuan et al., 2012) or in situ growth methods (Bao, Zang, & Li, 2011; Lei, Shi, & Lu, 2012; Yang et al., 2012), whereas carbon/polymer electrodes are prepared by electropolymerization (Ge, Cheng, & Chen, 2011; Horng et al., 2010; Wang et al., 2009) and chemical polymerization (Li, Gittleson, Carmo, Sekol, & Taylor, 2012; Meng, Liu, Chen, Hu, & Fan, 2010; Meng, Liu, & Fan, 2009; Yan, Tai, Chen, & Xue, 2011).

For example, MnO_2 was electrodeposited onto carbon fabric at an adequate current density in an aqueous solution (such as $Mn(CH_3COO)_2 + CH_3COONH_4$, $H_2SO_4 + MnSO_4$) followed by washing with deionized water (Chen et al., 2011; Kim, Lee, Overzet, & Lee, 2011; Yuan et al., 2012). The loading mass of MnO_2 is related to the deposited time. Chen et al. (2011) used MnO_2/carbon

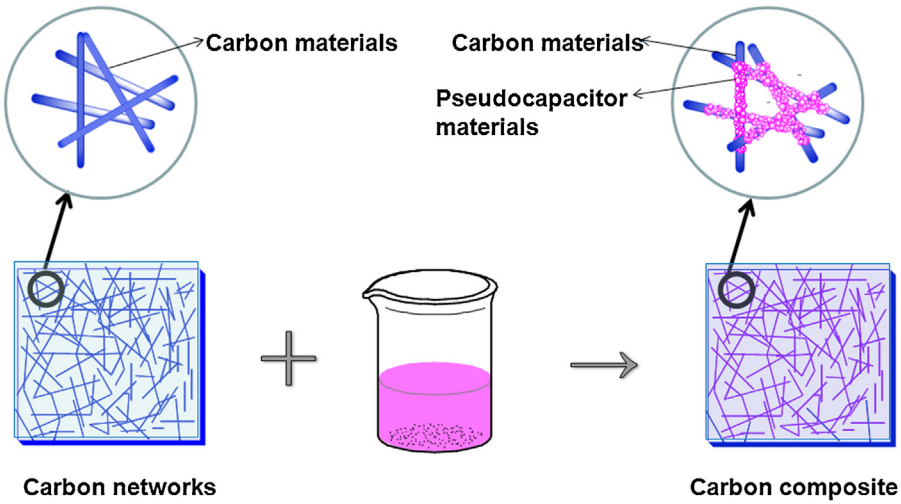

Fig. 3. Fabrication of carbon composites by coating pseudocapacitor materials onto carbon networks through a solution-based method.

composite electrodes to assemble highly flexible supercapacitors with a specific capacitance of 425 F/g. Yuan et al. (2012) demonstrated that a highly flexible solid-state supercapacitor with carbon nanoparticles/MnO_2 nanorods electrodes in polyvinyl alcohol (PVA)/H_3PO_4 electrolyte can obtain an energy density of 4.8 Wh/kg at a power density of 14 kW/kg. Lu et al. (2012) demonstrated that WO_{3-x}@Au@MnO_2 core–shell nanowires/CC electrodes exhibited an outstanding performance (588 F/g at a scan rate of 10 mV/s and 1195 F/g at 0.75 A/g), where the energy density can reach 106.4 Wh/kg at a power density of 23.6 kW/kg.

Polyaniline (PANI) has been electropolymerizated on carbon networks (such as CC, SWNT paper, and graphene paper) and achieved good electrochemical performance. Horng et al. (2010) fabricated flexible supercapacitors with PANI nanowires/carbon cloth electrodes resulting in a high capacitance (1079 F/g and 1.8 F/cm^2 for mass and area-normalized capacitance) and a high energy density (100.9 Wh/kg at a power density of 12.1 kW/kg).

In addition, carbon composite electrodes can also be created by similar methods to fabricate carbon paper. For example, Wu, Xu, Yao, Liu, and Shi (2010) reported that graphene/PANI nanofiber paper was produced by direct filtration of a dispersion consisting of graphene and PANI. The aqueous supercapacitor is assembled from graphene/PANI paper, exhibiting a specific capacitance of 210 and 198 F/g at a current density of 0.3 and 3 A/g, respectively.

Carbon composite electrodes take advantage of both the high conductivity of carbon networks and the pseudocapacitance properties of pseudocapacitor materials. Except for MnO_2 (Bao & Li, 2012; Chen et al., 2011; Hu, Chen, et al., 2011; Lei et al., 2012; Yuan et al., 2012) and PANI (Ge et al., 2011; Laforgue, 2011; Meng et al., 2009, 2010; Wang et al., 2009; Wu et al., 2010; Yan et al., 2011), other metal oxides, such as RuO_2 (Chen, Chen, et al., 2010), MnO_x (Chen, Shen, Shi, Chen, & Zhou, 2010; Kim et al., 2011), In_2O_3 (Chen, Shen, et al., 2010), CuO (Zhang et al., 2011), and Co_2O_3 (Yang et al., 2012), conducting polymers, such as polypyrrole (PPy) (Davies et al., 2011; Olsson et al., 2012), poly(3,4-ethylenedioxythiophene) (PEDOT) (Wu, Xu, Yao, Liu, & Shi, 2010), and polyurethane (PU) (Tai, Yan, & Xue, 2012), or metal oxides/conducting polymers composites (Chen, Sun, et al., 2010) have also been applied in carbon composite electrodes.

3. Flexible supercapacitors

The typical components of conventional supercapacitors are the outer packages, current collectors (metal foil), positive/negative electrodes, electrolyte, and a separator (Fig. 4(a)). The structure of flexible supercapacitors is simplified with no need for independent current collectors and binders (Fig. 4(b)) because the carbon network, with its high conductivity and flexibility, acts as both the active electrode and the current collector. Soft and bendable plastic (such as polybag, ethylene/vinyl acetatecopolymer (EVA) film, polyethylene terephthalate (PET), PDMS, and Telfon substrate) has been widely used as the package (Chen et al., 2011; Ge et al., 2011; Hu, Pasta, et al., 2010; Pushparaj et al., 2007; Yu et al., 2009). The simplified architecture is flexible and lightweight compared with the conventional supercapacitor.

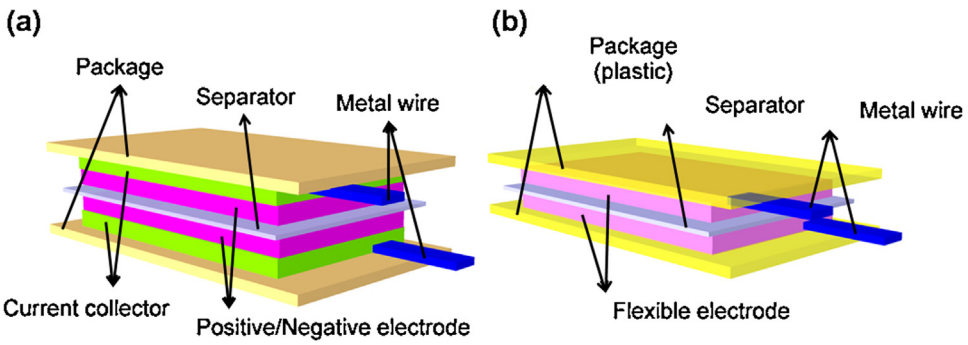

Fig. 4. Schematic illustrations of (a) a traditional supercapacitor and (b) a flexible supercapacitor.

Table 1
Electrolytes and separators used in flexible supercapacitors.

	Electrolyte species	Separator species
Liquid electrolyte	Aqueous solution: acid electrolytes (H_2SO_4 or H_3PO_4 solution), mild electrolytes (KCl, KNO_3, LiCl, Na_2SO_4 or Li_2SO_4 solution), and alkaline electrolytes (LiOH, NaOH or KOH solution) Organic: 1 M $LiPF_6$ in EC/DEC, 1 M $LiPF_6$ in EC/PC/DMC, 1 M Et_4NBF_4/PC	Filter paper, glassy paper, cellulose, polyacrylonitrile membrane
Solid-state electrolyte	H_3PO_4/PVA, H_2SO_4/PVA, $EMIBF_4$/P(VDF-HFP), Nafion membrane	Paper

Single carbon electrodes and carbon composite electrodes serve as positive or negative electrodes depending on the design. Generally, according to the used electrode materials, the supercapacitor can be classified as a symmetric supercapacitor, in which both electrodes are identical, or an asymmetric supercapacitor, in which the two electrodes are different. The asymmetric design with its high working voltage leads to a high energy density. For example, a flexible asymmetric supercapacitor used MnO_2–SWNT and In_2O_3–SWNT electrodes as the cathode and anode, respectively, and exhibited a specific capacitance of 184 F/g with an energy density of 25.5 Wh/kg in an aqueous electrolyte (Chen, Shen, et al., 2010). Yu et al. (2011) successfully assembled an asymmetric supercapacitor with graphene/MnO_2-textile and SWNT-textile as the positive and negative electrode, respectively. The specific capacitance reached up to 315 F/g. Recently, an asymmetric supercapacitor with good flexibility and electrochemical performance achieved a specific capacitance of 120 F/g and a high energy density of 66.7 Wh/kg (Bao & Li, 2012).

In addition to the electrodes, the other important component is the electrolyte. The electrolyte used in flexible supercapacitors can be divided into two categories: liquid electrolytes (including aqueous liquid electrolyte and organic electrolyte) and solid electrolytes (as known as a polymer electrolyte). Liquid electrolytes are aqueous or organic solutions. Aqueous electrolytes can be acid electrolytes (for example, H_2SO_4 or H_3PO_4 aqueous solution), mild electrolytes (for example, KCl, KNO_3, LiCl, Na_2SO_4, or Li_2SO_4 aqueous solution), or alkaline electrolytes (for example, LiOH, NaOH, or KOH aqueous solution) (Chen, Shen, et al., 2010; Horng et al., 2010; Kaempgen et al., 2009; King, Higgins, De, Nicoloso, & Coleman, 2012; Masarapu et al., 2012; Meng et al., 2009). Organic electrolytes generally use a mixture of a salt dissolved in an organic solvent. 1 M $LiPF_6$ in ethylene carbonate/diethylene carbonate (EC/DEC = 1:1) or EC/PC/DMC (1:1:1) and 1 M Et_4NBF_4/PC solutions are widely used as organic electrolytes (Hu et al., 2009; Hu, Wu, & Cui, 2010; Izadi-Najafabadi et al., 2011; Kang et al., 2012; Torop et al., 2011; Yu et al., 2009). Solid-state electrolytes are usually synthesized by a sol–gel method.

A solid-state electrolyte is generally a mixture of a gel agent, a solute and a solvent. The gel agents are PVA, PVDF, or poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)). As an example, we will use the H_3PO_4/PVA solid-state electrolyte. PVA is dissolved in water. Then, H_3PO_4 is added to the PVA/water to form the solid-state electrolyte. A solid electrolyte has great potential in future transparent, flexible energy storage devices due to its safety and with no need of a separator (Chen, Chen, et al., 2010; Kaempgen et al., 2009; Lu et al., 2012; Meng et al., 2010; Torop et al., 2011; Xue et al., 2011; Yoo et al., 2011). The electrolytes and separators used in flexible supercapacitors are listed in Table 1.

Electrolytes for flexible supercapacitors with single carbon electrodes are extremely rich. In supercapacitors with carbon/metal oxide composite electrodes, the most commonly used electrolytes are aqueous Na_2SO_4 liquid electrolytes and PVA/H_3PO_4 (sol–gel). In supercapacitors composed of carbon/polymer composite electrodes, only PVA/H_3PO_4 and H_2SO_4/PVA electrolytes are available.

4. Prospects

With the boost of flexible, transformable, and/or bendable consumer electronics, our society requires supercapacitors to be diverse and colorful. Flexible and/or transparent supercapacitors are certainly the best solution to meet the specific needs of future consumer electronics. It is urgent to develop the "next-generation" supercapacitor with flexible and/or transparent properties. Currently, flexible supercapacitors are being widely investigated to determine whether they can be the power sources for new flexible consumer electronics. Electrodes in flexible supercapacitor are typically composed of a carbon network as the infrastructure. Carbon networks are highly conductive, binder-free and flexible. The advantage of using flexible carbon networks as the electrodes is that it is unnecessary to use metal foils (normally Al foil) as the current collector, polymers as the binder, and carbon materials as the conductive additive. The electrode is comprised of 100% active materials, which are involved in the electrochemical reaction for energy storage. These advantages enable the flexible supercapacitor to be lighter, thicker, and easier to be manufactured than conventional supercapacitors. To further improve the performance of the electrode composed of pure a carbon network, metal oxides (such as RuO_2, MnO_x, In_2O_3, CuO or Co_2O_3) and conducting polymers (such as PPy, PEDOT or PU) have been designed to be deposited onto the carbon infrastructure. The combination of the carbon network with the pseudocapacitive materials significantly increases the capacitance of flexible electrodes.

Despite all of these achievements, effort must still be delivered. The electrode is the key to the supercapacitor. Flexible electrodes are only made from carbon-based materials. It is well known that the capacitance of carbon materials is lower than that of pseudocapacitive materials. Therefore, to further increase the capacitance of electrodes, the mass content of carbon must be controlled to be as low as possible. However, it is still necessary to maintain a high conductivity of the electrode to obtain a high power density. The thickness of the electrode is an important parameter in the manufacturing of supercapacitors. However, controlling the thickness of flexible electrodes synthesized by state-of-the-art methods is still a problem. Therefore, a new, simpler method needs to be developed to synthesize flexible electrodes with a high specific capacitance, high conductivity, and stability through a controlled process.

As described in the previous section, currently, we do not have many choices when choosing separators and electrolytes for flexible supercapacitors. Today, much effort is being made to develop flexible electrodes. However, the electrolyte and separator seem to be ignored. In the future, specific electrolytes and separators for flexible supercapacitors must be developed.

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