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Carbon nanomaterials for flexible lithium ion batteries

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ABSTRACT

With the rapid progress of wearable electronics, it is highly desirable to develop flexible power supplies, and significant progress has been thus made in making a variety of flexible batteries. Here the recent advances of flexible lithium ion batteries based on carbon nanomaterials have been carefully discussed from the viewpoint of material synthesis, structure design and property optimization. The remaining challenges and promising directions are highlighted to provide the clues for the future study in this booming field at end.

1. Introduction

The deepening energy crisis has forced people to find sustainable energy harvesting and storage systems that are low-cost, reliable and environmentally friendly [1–3]. The past three decades have witnessed the dramatic progress in developing electrochemical energy storage systems such as lithium ion batteries (LIBs) for the wide applications ranging from portable electronics, electric vehicles and spacecraft to grid-scale smart energy storage systems [4–7]. On the other hand, the emerging promising directions in electronics such as wearable electronics, smart clothes, electronic papers, electronic skins, robots and implantable medical devices are regarded as the next-generation revolution, and may open up novel application directions for future lifestyles [8–11]. To work stably in close contact with the human body, the related electronic devices above are needed to be flexible, foldable, bendable and even stretchable. As a result, the indispensable power systems should also meet these requirements.

LIBs are used as one of the most common power supplies because of their high energy density, long cycle life and high working voltage [12,13]. Conventionally, LIBs are heavy and rigid based on the currently available materials, fabrication processes and traditional configurations [14,15]. More specifically, LIBs consist of various chemical substances, including cathode materials (e.g., $LiCoO_2$, $LiMn_2O_4$ or $LiFePO_4$), anode materials (e.g., graphite, $Li_4Ti_5O_{12}$ or silicon), conductive materials (e.g., carbon black), binders, current collectors (e.g., aluminum and copper foil), separators, electrolytes and packaging materials [16–18]. The cathode and anode are prepared by coating slurry containing active material, binder and conductive material on the surfaces of aluminum and copper foils, respectively. Due to low elastic limits of metal foils, these electrodes are unable to accommodate drastic deformations. Once encountering a deformation that is beyond the critical point, a permanent change of the structure and degradation of electrochemical performance will occur. Due to the poor adhesive attraction between active materials and metal foils, the active materials are also easy to detach from metal foils and thus fail to work under deforming. In addition, conventional LIBs usually appears in bulk or cylinder structure, which may cause stress accumulation and further permanent destruction during deformation [14].

The synthesis of novel electrode materials, design of new structures, and optimization of fabrication processes are recognized as three main strategies to realize the flexibility of LIBs. Since the traditional electrode components are not deformable enough, it is highly desired to replace them by new candidates that should satisfy the following facts: (i) they should be highly electrically conductive to rapidly transfer electrons; (ii) the active materials are expected to be stably anchored on the supporting substrate with high loading capacity; (iii) they should be highly flexible and strong, and remain stable under deformations; (iv) they should exhibit high electrochemical performances.

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Carbon nanomaterials such as 1D carbon nanotube (CNT) and 2D graphene have attracted increasing interests due to their unique structures and high mechanical, electrical and electrochemical properties [19,20]. Flexible 3D sponge-like, 2D paper-like and 1D fiber-shaped LIBs and stretchable LIBs have been widely explored from the above carbon nanomaterials, and a brief chronology of the development in flexible and stretchable LIBs is shown in Fig. 1. In this review article, the advances of novel carbon nanomaterials in the aspect of synthesis, structure and property are first summarized, the application of them in flexible and stretchable LIBs is then highlighted with an emphasis on the structure control and property optimization, and the major challenges in flexible LIBs are finally discussed to provide some useful insights for the future development.

2. Carbon nanomaterials

Carbon nanomaterials composed of sp^2 conjugated carbon atoms have various allotropes with their matching microscopic architectures and assembling forms, which possess promising applications for flexible energy storage. Compared with the widely studied metallic materials, carbonaceous materials are endowed with lower mass density and higher intrinsic flexibility derived from microscopic structures (Table 1). Besides, their high chemical stability and wide potential window also avoid corrosions and benefit the cyclic reversibility. In addition, abundant reaction sites and high specific surface areas in carbonaceous nanomaterials facilitate stable loading of active materials for high electrochemical performances [28].

Among allotropes of carbon nanomaterials, CNT and graphene demonstrate significantly desirable properties and are promising in building flexible batteries. CNT, revealed as a seamless cylinder composed of carbon atoms with unique structural chirality, has been demonstrated important in modern electronics due to the expected metallic or semiconducting electronic properties and superior mechanical properties, which make it very useful for flexible energy storage devices. Graphene is a kind of honeycomb-liked 2D materials composed of monoatomic layer of carbon atoms and possesses high stiffness, electrical conductivity and thermal conductivity. Extending the afore-mentioned high properties of CNT and graphene from nanoscale to macroscopic scale remains a key while a big challenge in the construction of flexible energy storage devices. Herein, the corresponding macroscopic materials in three different dimensions composed of CNT and graphene are summarized by preparation methods, properties and applications.

2.1. 3D materials

3D architecture materials composed of CNT and graphene usually display high aspect ratios and tunable porous structures. The loosely compacted architectures and the highly tunable inner spaces endow 3D materials with great features of being lightweight and compressible, which are of importance for flexible energy storage systems.

For CNT materials, 3D architectures can be obtained mainly by wet gel-initiated method and template-directed assembling method. The former strategy is realized *via* the self-gelation behavior of CNT [36]. More specifically, CNT gels or sols are uniformly prepared in aqueous conditions as precursors, and frameworks are produced *via* the interactions among neighboring CNT bundles. Followed by freeze drying or supercritical drying process, solvents trapped among voids are removed, thus facilitating the formation of CNT materials with 3D architectures. The stabilization and enhancement of CNT skeletons are important for flexible energy storage devices [37]. The template-directed assembling methods are more facile and environmentally friendly (i.e., employing ice or cube sugar as templates) [38]. Highly orientated porous CNT materials can be obtained through the process of matching cryogen to produce high specific capacities when they were used as electrodes for batteries (Fig. 2a and b).

Graphene materials also tend to form loosely compacted 3D architectures. It is noteworthy that the inner walls need to be composed of single or several layers of graphene sheets to form 3D architectures with high aspect ratios and void ratios. Graphene oxide (GO) is widely adopted as the precursor to prepare 3D graphene materials. Apart from wet methods like CNTs, 3D graphene materials can be also obtained *via* hydrothermal methods, based on which functional components or heterogeneity atoms can be incorporated into or doped onto graphene sheets prior to hydrothermal reactions [39]. The 3D graphene foams can be also prepared by template-directed chemical vapor deposition. The obtained graphene foams consist of an interconnected network of graphene sheets with high electrical conductivity, light weight and flexibility (Fig. 2c and d) [22]. Several strategies for fabricating CNT/

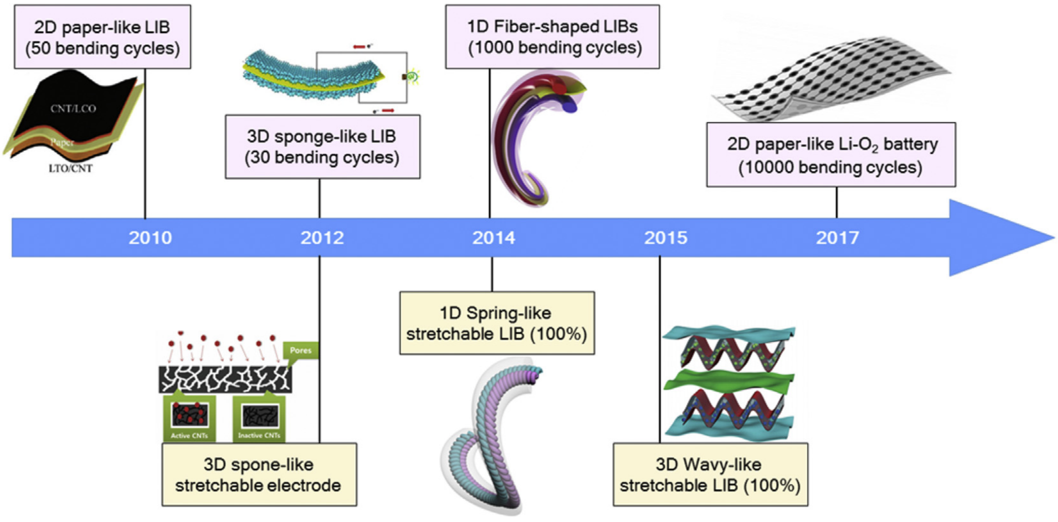

Fig. 1. A brief chronology of the development of flexible and stretchable LIBs [21–27]. (A colour version of this figure can be viewed online.)