Pursuing two-dimensional nanomaterials for flexible lithium-ion batteries

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Summary Stretchable/flexible electronics provide a foundation for various emerging applications that beyond the scope of conventional wafer/circuit board technologies due to their unique features that can satisfy a broad range of applications such as wearable devices. Stretchable electronic and optoelectronics devices require the bendable/wearable rechargeable Li-ion batteries, thus these devices can operate without limitation of external powers. Various two-dimensional (2D) nanomaterials are of great interest in flexible energy storage devices, especially Li-ion batteries. This is because 2D materials exhibit much more exposed surface area supplying abundant Li-insertion channels and shortened paths for fast lithium ion diffusion. Here, we will review the recent developments on the flexible Li-ion batteries based on two dimensional nanomaterials. These researches demonstrated advancements in flexible electronics by incorporating various 2D nanomaterials into bendable batteries to achieve high electrochemical performance, excellent mechanical flexibility as well as electrical stability under stretching/bending conditions.

Keywords

Two-dimensional; flexible batteries; nanomaterials; potential application

1. Introduction

Increasing demands for high-efficiency, environmentally friendly and low-cost energy sources are associated with the increase concern on energy independence and environment concerns [1-9]. Among various energy storage systems, rechargeable lithium-ion batteries are one of the most promising power sources to alleviate energy crisis [10-15]. Although significant progresses have been made on Li-ion batteries (LIBs) in the last a few decades, most of these batteries are still short of features of such as flexibility, bendability, wear-ability, which forms a barrier for the development of next-generation flexible optoelectronic products [16-24]. The increasing interest in flexible and stretchable electronics has promoted the rapid development of flexible batteries. Here, all these components (including cathode, anode, electrolyte, separator, and packing material) in a flexible battery need to be flexible and bendable. The paramount goal of on-going research on flexible batteries is to smoothly maintain the expected battery stability under various bending states. Moreover, different curving and stretching level of flexible rechargeable batteries would be designed and fabricated, depending on their various application fields, while the traditional batteries are rigid with certain shapes. Thus, significant efforts are being made around world to fabricate highly flexible rechargeable batteries [25-35].

To overcome the tremendous challenge of fabrication of highly stable flexible Li-ion batteries, utilizing nano-structure materials to prepare electrodes is one of the most promising strategies. It is well-known that nanomaterials can be classified in four categories: zero dimensional (0D), one dimensional (1D), two dimensional (2D), and three dimensional (3D). Here, 0D structures (nano/microsphere) hold the minimum surface area, and exhibit excellent thermal stability. 1D structures (nanotubes/nanowires) fabricated by oriented growth have a potential application for micro-devices. 2D structures (nanosheets) often have large exposed surfaces, and specific facets.

In general, 3D structures could be obtained by introducing structure directing agents (SDAs) or assembled by 0D, 1D, and 2D structures [36]. In particular, comparing to 0D, and 1D nanomaterials, 2D nanomaterials exhibit many unique features, such as small weight, large surface area, sensible distribution, more active sites with effective surface. Therefore, it would be highly desirable to use 2D nanomaterials in the design and preparation of flexible energy storage devices.

In this review, we will focus on advances on typical two-dimensional (2D) functional materials for flexible/bendable lithium-ion batteries, such as flexible 2D graphene paper, various graphene-based composite cathodes and anodes, 2D **inorganic** nanosheets, etc, as shown in Fig. 1. How to better understand the selection, design, and optimization of these aforementioned bendable and free-standing electrodes should be a key sweet spot for next-generation flexible LIBs chemistries. It is expected that this overview will not only summarize the highlighted developments of 2D nanomaterials-based flexible energy storage field but also shine light on the directions for further development of 2D functional nanomaterials for various applications.

2. Flexible two dimensional graphene-based electrodes for Li-ion batteries

Recently, more and more interests were focused on portable and bendable electronic units such as roll-up displays, wearable devices, and implanted medical devices [37,38]. However, the design and fabrication of bendable batteries is facing a significant challenge: how to find reliable flexible materials with robust strength, good conductivity, and excellent electrical stability under bending. Among two-dimensional materials, graphene is an atom-thick two-dimensional carbon sheet. The σ carbon-carbon bond is the strongest single bond in nature, resulting in graphene with high Young's modulus and tensile strength [39]. Therefore, graphene as active material was

also smoothly introduced into high performance flexible energy storage devices due to their potential superiority in terms of mechanical flexibility and charge-carrier mobility [40].

2.1 Flexible **two-dimensional** graphene paper

Graphene paper has dual functions and can act both as a conducting agent and a current collector. Clearly, based on graphene's features, the graphene paper itself holds some unique properties, making it a key factor for development of flexible LIBs [41-44]. Fabrication of graphene papers have been reported previously [41,43-45]. Briefly, it is well-known that graphite oxide can be synthesized from graphite powder by oxidation using a typical Hummers method [46]. Then, graphene paper was usually fabricated by filtration of graphene dispersions [41,43-45,47]. Koratkar et al. introduced photothermal reduction of graphene oxide to obtain graphene paper anodes, the corresponding procedures and characterizations are shown in Fig. 2a-2d [44]. Clearly, a free-standing graphene paper exhibits good bendable features (Fig. 2c) so it is a good candidate to be used in flexible-batteries. In Fig. 2e, these flexible graphene paper electrodes showed excellent cycling stability over 1000 discharge/charge times and high rate capability (20 C, 40 C, 100 C, and 150 C). Clearly, extensive developments of graphene papers will trigger more research on flexible optoelectronics in the near future. Liu et al. fabricated the flexible graphene paper made from the graphene aerogel pre-synthesized by freeze-drying a GO aqueous dispersion and subsequent thermal reduction [48]. The free-standing graphene paper shows excellent flexibility as shown in Fig. 3a-3c. The well-packed layers can be observed in the whole paper sample (Fig. 3d). The fracture edge of a graphene paper sample is revealed in the inset of Figure 1d, which demonstrates well stacked graphene sheets. In addition, flexible graphene paper indicates enhanced cyclic stability (over 100 times), and good rate capability (Fig. 3e and 3f),

thus providing a possibility to act as a new kind of flexible electrode for wearable/rolling-up optoelectronics devices.

2.2 Flexible **two-dimensional** graphene composite **paper** anodes

Considering 2D graphene sheets with a large surface, these graphene sheets can serve as a building template to compose other active materials to form various flexible functional electrodes. Lots of flexible graphene/active material composite **anodes**, such as flexible graphene/TiO₂ **nanoparticles composite** paper [49,50], graphene/Co₃O₄ **fibers composite** paper [51], graphene/SnO₂ **nanoparticles** paper [52], graphene/MnO₂ nanotube hybrid film [53], have been developed. **Most functional materials were deposited onto pre-obtained graphene paper via hydrothermal, filtration, immersion followed by thermal decomposition methods [50-54].** For example, Hu et al. reported an ex-situ method to prepare a flexible graphene/TiO₂ **nanoparticles** hybrid paper electrode [49]. Because of the highly conductive graphene network, the flexible composite paper electrode reaches a capacity of 122 mA h g⁻¹ at 2 A g⁻¹ after 100 cycles. Surface structure is considered as a key factor to determine the rate of the Li⁺ ion de-intercalation/intercalation process. Yang et al. fabricated **Co₃O₄ fibers using electrospinning technique, then got** graphene/Co₃O₄ **fibers** composite papers by depositing graphene nanosheets on Co₃O₄ active materials via electrostatic interaction, indicating a large reversible capacity (840 mAh g⁻¹ after 40 cycles), and improved cycling stability [51]. Liang et al. prepared flexible free-standing graphene/SnO₂ nanocomposite papers by a facile filtration route together with a thermal reduction [52]. To utilize unique respective advantages of SnO₂ and graphene, the SnO₂ nanoparticles are embedded into layers of 2D graphene sheets, two layers including SnO₂ nanoparticles and graphene sheets are distributed uniformly, as shown in different magnification FESEM cross-section and top-view images (Fig. 4a-4e). An as-synthesized free-standing

SnO₂/graphene film can be bent by a tweezer, thus indicating its excellent flexibility (Fig. 4f). Although graphene/SnO₂ composite electrodes exhibited a low capacity during the first few cycles due to poor electrolyte wetting of the dense graphene/SnO₂ paper, their corresponding discharge capacity still reach 428 mAh g⁻¹ after 50 cycles (about 83.4 % retention those at 25th cycle), as illustrated in Fig. 4g. In contrary, bare SnO₂ electrodes delivered poor cycling stability. Fig. 4h shows that the graphene/SnO₂ electrode in the high-medium frequency region exhibits a much smaller charge transfer resistance than that of the SnO₂ electrode (as revealed by a much smaller diameter of the semicircle in the impedance spectra of the graphene/SnO₂ electrode). Huang et al. loaded the transition-metal oxides (Fe₃O₄, Co₃O₄, and NiO) into the nanoporous graphene papers via a general wet-immersion route to form free-standing flexible composite papers. These flexible composite electrodes exhibited enhanced electrochemical performance [54].

Beside above binary inorganic materials, because silicon has very high theoretical capacity (4200 mAh g⁻¹), it has been combined with graphene with unique features to synthesize bendable free-standing hybrid **anodes** for flexible Li-ion batteries [55-57]. For example, Wang et al. proposed fabrication of flexible and paper-like graphene-silicon composites by a one-step *in-situ* filtration method [58]. The flexible graphene-Si composite electrodes showed much higher discharge capacity over 100 cycles (708 mAh g⁻¹) than that of the graphene electrodes (304 mAh g⁻¹). Here, 2D graphene can serve as a flexible mechanical and efficient electrically conducting support. In addition to flexible two-component (graphene-Si) electrode, flexible binder-free SiNW@G@RGO hybrid materials were also designed [56]. **Firstly, SiNW@G nanocables were grown via chemical vapor deposition (CVD) approach. Then, SiNW@G nanocables were dispersed in GO solution. The homogeneous mixture was vacuum filtered, peeled from the filter**

membrane. Finally, flexible SiNW@G@RGO composite anodes were obtained after thermal treatment. The morphologies of as-fabricated SiNW@G@RGO can be found in Fig. 5a-5d. In addition, compared to two other electrodes based on SiNW@G and SiNW, flexible SiNW@G@RGO electrodes exhibit higher reversible specific capacity of over 1500 mAh g⁻¹ at 840 mA g⁻¹ (Fig. 5e), and even reach 1600 mAh g⁻¹ at 2.1 A g⁻¹ with 80% capacity retention after 100 cycles (Fig. 5f).

2.3 Flexible two-dimensional graphene composite cathodes

In addition to composite anodes, various cathode materials were also incorporated into 2D graphene films by using catalyst assisted self-assembly, co-precipitation, pulsed laser deposition (PLD), microwave hydrothermal, and photothermal reduction methods [59,60,62-64]. These composite cathodes include graphene/LiFePO₄ nanoparticles [59-61], graphene/V₂O₅ films [62], graphene/MoO₃ nanobelts [63], and graphene/FeF₃ nanoparticles [64]. Li et al. proposed a new design of flexible batteries based on Li₄Ti₅O₁₂ (LTO)/graphene form (GF) and LiFePO₄ (LFP)/GF electrodes by hydrothermal deposition of active materials on GF followed by heating in an argon atmosphere [61]. Fig. 6a shows the TEM images of LTO nanosheets/graphene composites. LTO nanosheets are several hundred nanometers in width and a few nanometers in thickness (Fig. 6b). Further, a LTO/GF electrode was combined with a LFP/GF to form a flexible full Li-ion battery (Fig. 6c). This flexible battery can smoothly drive a red LED even under bending condition, as shown in Fig. 6d. From Fig. 6e and Fig. 6f, it can be seen that the discharge/charge curves and cyclic stability of flexible battery are barely affected by external bendable stress, thus demonstrating its good flexible electrical stability. Moreover, Gwon et al. reported a flexible Li-ion battery composed of bendable graphene paper and V₂O₅/graphene paper as anode and

cathode, respectively, as illustrated in Fig. 7a-7c [62]. Here, the graphene paper made via a vacuum filtration and V_2O_5 films can be grown onto graphene paper by using a pulsed laser deposition (PLD) in a vacuum chamber. The flexible battery can be discharged and charged when rolled up, revealing its potential feasibility in flexible electronics (Fig. 7b). The V_2O_5 /graphene paper electrode showed better performance in terms of capacity, rate capability as well as cycling life, compared to non-flexible traditional V_2O_5 /Al foil electrode (Fig. 7d and 7e). In addition, Noerochim et al. introduced highly flexible binder-free MoO_3 nanobelt/graphene film electrode into fabrication of bendable Li-ion batteries via a two-step micro-wave hydrothermal method [63]. The as-prepared flexible MoO_3 /graphene hybrid electrodes showed excellent rate capability, enhanced capacity, and superior cyclic stability, compared to the sole MoO_3 electrodes. The progresses in flexible 2D graphene-based composite cathodes can be combined with graphene-based composite anodes mentioned above.

3. Flexible two-dimensional inorganic nanosheets-based electrodes for Li-ion batteries

With rapid development of battery technology, the scope of 2D nanosheets used in energy storage devices is not limited only to above graphene sheets. Recently, many promising 2D inorganic nanomaterials were further developed as well since 2D sheet-like nanomaterials with unique characteristics illustrated excellent electrochemical properties for energy storage devices. In particular, most researchers focused on flexible electrodes based on oxide nanosheets, sulfide nanosheets, multiple-compound nanosheets for future bendable lithium-ion batteries.

3.1 Flexible two-dimensional oxide nanosheets composites

In general, preparation of oxide nanomaterials can be regarded as a facile, environment-friendly,

low-cost route. Many efforts on fabrication of oxide nanosheets have been disclosed for lithium-ion batteries, such as porous NiO nanosheets/graphene synthesized by electrostatic interaction [65], porous Fe_2O_3 nanosheets synthesized by solvothermal approach followed by annealing [66], porous Co_3O_4 nanosheets synthesized by hydrothermal process [67], polythiophene (PTh)-coated MnO_2 nanosheets prepared by aqueous/organic interfacial synthesis [68], SnO_2 nanosheet arrays/Ti foil prepared by solution method followed by annealing [69]. Compared to the 2D nanosheets applied in the traditional non-flexible energy devices, only a few literatures regarding oxide nanosheets for flexible Li-ion batteries were reported. For example, Li et al. proposed the an anisotropic flexible electrode fabricated by controlling the growth of TiO_2 nanosheets parallel to the surface of the graphene paper, which results in the Li^+ ion insertion and diffusion being anisotropic, as shown Fig. 8a and 8b [70]. The optical image shows an as-synthesized anisotropic flexible electrode (Fig. 8c). TiO_2 sheets directly were grown on graphene paper to form a flexible anode, as shown in Fig. 9d. The cycling performance at 10 C between the TiO_2 nanosheets/graphene and TiO_2 spheres/graphene electrodes, TiO_2 nanosheets/graphene anodes delivered around 150 mAh g⁻¹ over 100 cyclic times, which exhibits superior cyclic stability than TiO_2 spheres/graphene composites (Fig. 8e). This is consistent with above-mentioned cell operation schematic of both TiO_2 samples (Fig. 8a and 8b). Also, Liu et al. designed TiO_2 nanosheets/activated carbon fabric (ACF) electrodes [71]. Firstly, fabrication of the ACF by electrospinning and thermal activation in CO_2 was conducted. Then, TiO_2 (B) nanosheets were deposited onto carbon fabric film using hydrolysis approach followed by thermal annealing. The photograph of an as-prepared electrode shows its free-standing, flexible properties (Fig. 9a). These bendable electrodes can be easily punched into disc electrodes to fit for the coin-cell size, as shown in Fig. 9b. Clearly, numerous fibers from non-woven ACF were coated with 2D

uniform TiO₂ nanosheets, thus facilitating enhancement in electrical contact between TiO₂ active materials and carbon substrate (Fig. 9c-9e). The charge/discharge profiles of TiO₂ (B)/ACF electrodes indicate the large capacity loss in the first cycle due to the interfacial reaction between TiO₂ (B) and the LiPF₆-based electrolyte, which should be common phenomenon for most lithium-intercalation hosts (Fig. 9f). After 1000 cycles, the specific capacity of TiO₂ (B)/ACF electrodes still be close to 200 mAh g⁻¹ (85% capacity retention). Corresponding coulombic efficiency (CE) can maintain around 100 % as well, except for initial several cycles (Fig. 9g). From this plot, it can be also seen that the contribution of bare ACF to total capacity is negligible. Compared to anatase TiO₂ nanoparticles-based electrodes, TiO₂ (B) nanosheets/ACF electrodes demonstrate enhanced rate-capability, as well as even hold stable cycling at 20 C for 2000 cycles (Fig. 9h, and 9i, respectively). In this study, this type of flexible electrodes would hold a great potential for the development of flexible energy storage units with high power and energy densities.

Moreover, Liu et al. proposed a free-standing flexible CuO nanosheets (NSs)/r-GO composites fabricated by a vacuum filtration method and hydrothermal reduction process, as illustrated in Fig. 10a [72]. CuO NSs can be uniformly incorporated between r-GO layers, which seem like layer-by-layer sandwiched architecture (Fig. 10b and 10c). Within, r-GO layers can act as mechanical supporting and current collector. Fig. 10c inset demonstrates the photo of as-obtained highly flexible CuO NSs/r-GO composite electrode. Corresponding cyclic performance of CuO NSs/r-GO, bare CuO NSs, bare r-GO electrodes at a current density of 67 mA g⁻¹ (Fig. 10d). These CuO NSs/r-GO flexible electrode can deliver the highest retaining discharge capacity (736.8 mAh g⁻¹), which is much higher than that of CuO NSs-based electrodes. In addition, the discharge capacity of bare r-GO electrode is close to 60 mAh g⁻¹ after 50 cycles, thus revealing

that the total discharge capacity of CuO NSs/r-GO electrode should be mainly attributed to contribution of CuO NSs.

3.2 Flexible two-dimensional sulfide nanosheets composites

In addition to the 2D oxide-based nanomaterials, fabrication of many sulfide-based 2D materials applied for rechargeable Li-ion batteries also attracted significant attentions. Here, MoS₂ has been considered as a potential candidate for electrode materials in Li-ion batteries due to its layered structure and high theoretical capacity. Thus, many interesting MoS₂ nanosheets-based electrodes were synthesized using glucose-assisted hydrothermal method [73], solvothermal reaction at a low temperature [74], template-assisted strategy [75], hydrothermal process followed by annealing [76], coprecipitation combined with solvothermal route [77]. Furthermore, SnS₂ nanosheets/MWCNTs coaxial nanocables were prepared via a modified layer-by-layer assembly approach [78].

It is highly expected that some functional 2D sulfide nanosheets have been introduced into the studies on the flexible electrodes for potential bendable lithium-ion batteries. Li et al. deposited 2D MoS₂ nanosheets onto the carbon nanotube paper by a hydrothermal method to achieve flexible free-standing composite electrodes (Fig. 11a) [79]. From Fig. 11b and 11c, it can be seen that MoS₂ nanosheets were uniformly incorporated with carbon nanotubes. Fig. 11d shows the EDX mapping images of the elements carbon, molybdenum, and sulfur, it can be seen that the homogeneous distribution of molybdenum and sulfur is well matched with the outline of the carbon nanotube. Additionally, the MoS₂ nanosheets/carbon nanotube paper electrodes indicated a higher capacity of 1053, 1040, 1014, 975, 918, 856, 762, and 684 mAh g⁻¹ at a current density of 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10 A g⁻¹, respectively, as shown in Fig. 11e. This

reflects the superior rate capability of MoS₂ nanosheets/carbon nanotube paper electrodes, compared to that of control bulk MoS₂ electrodes. After 100 cycles, the discharge capacity of MoS₂ nanosheets/carbon nanotube paper electrodes still be close to 1100 mAh g⁻¹ with a capacity retention of 90% for the initial discharge capacity (Fig. 11f). In comparison, these bulk MoS₂ electrodes showed rapidly capacity-fading during 100 cycles. High performance MoS₂ nanosheets/carbon nanotubes composite electrode would hold a potential application for flexible Li-ion batteries.

In the recent literature, Balogun et al. proposed a vanadium nitride supported SnS₂ nanosheets flexible electrodes for lithium-ion batteries [80]. Briefly, a highly flexible carbon cloth (CC) film was firstly coated vanadium nitride (VN) nanowires through hydrothermal and annealing processes. Then, as-obtained CC-VN composite was immersed into a solution of SnCl₄ and L-cysteine at 180 °C for 6h to make SnS₂ nanosheets coated onto the CC-VN surface. The total two-step growth process can be found in Fig. 12a. The corresponding SEM and optical images of bare CC, CC-VN, and CC-VN/SnS₂ are also provided in Fig. 12b and its inset, Fig.12c and its inset, and Fig. 12d and its inset, respectively. Considering well-known woven carbon cloth substrate with excellent flexibility, carbon cloth coated VN/SnS₂ still can hold bendable/stretchable features for potential application in flexible Li-ion batteries. Clearly, CC-VN/SnS₂ nanosheets electrodes indicate excellent cyclic stability (up to 100 cycles), as shown in Fig. 12e. After 100 cycles, the discharge capacity of CC-VN/SnS₂, CC-VN, and CC-SnS₂ electrodes are 791 mAh g⁻¹, 322 mAh g⁻¹, and 270 mAh g⁻¹, respectively. Moreover, the CC-VN@SnS₂ electrodes show superior rate capability over the CC-VN, and CC-SnS₂ electrodes (Fig. 12f).

3.3 Flexible two-dimensional multiple-compound nanosheets composites

Recent progresses in multiple-compound nanosheets as electrodes for lithium ion batteries, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets [81,82], $\text{Li}_2\text{FeSiO}_4$ ultrathin nanosheets [83], and LiFePO_4 nanosheets [84], have already been disclosed. The multiple-compound containing two or more types of metal ions deliver enhanced electrochemical performance due to their synergetic effects upon charge-discharge process [85,86]. Further, with the rapid development of traditional non-flexible Li-ion battery based multiple-compound nanosheets, some multiple-compound nanosheets-based flexible electrodes were also successfully achieved. For example, Xiong et al. designed all-nanosheet-based Li-ion full battery using ZnMn_2O_4 -graphene hybrid nanosheet and LiFePO_4 nanosheet as anode and cathode [87], respectively, on basis of previous synthesized methods [88,89]. ZnMn_2O_4 nanocrystals were well dispersed on the surface of 2D graphene nanosheets to form ZnMn_2O_4 -graphene composite nanosheets, as shown in Fig. 13a. The as-synthesized LiFePO_4 nanosheets with thickness of 30~60 nm have uniform morphology (Fig. 13b). Further, Fig. 13c indicates the galvanostatic discharge/charge measurements, which reveals that the 2D ZnMn_2O_4 -graphene composite electrodes delivered much larger specific capacity, enhanced rate capability and superior cyclic stability, compared to those of traditional graphite electrodes. Moreover, authors moved the LiFePO_4 nanosheet cathodes into the half-cells to measure rate capability, as disclosed in Fig. 13d. Compared to commercial LiFePO_4 , 2D LiFePO_4 nanosheets showed better rate performance due to the LiFePO_4 nanosheets with high oriented $\{0\ 1\ 0\}$ surface could supply increased active surface area and shortened Li^+ diffusion pathways [90,91]. Based on these half-cells, the 2D ZnMn_2O_4 -graphene composite anode and 2D LiFePO_4 nanosheets cathode were transferred into flexible/bendable full Li-ion batteries. This flexible battery exhibited excellent electrochemical stability without structural failure and capacity/CE loss under various mechanical bending states (Fig. 13e-13i). In addition to above all-nanosheet-

based flexible batteries, Hou et al. conducted successfully 2D MnCo_2O_4 nanosheets grown on the highly stretchable carbon cloth **using hydrothermal method** for flexible Li-ion batteries [92]. The binder-free MnCo_2O_4 nanosheets/carbon cloth composite electrodes delivered stable cycle life (over 60 times), enhanced rate capability, as well as highest areal capacity than that reported in previous literatures [93-95].

Using a simple and scalable process, Li et al. synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) nanosheets with N-doped carbon coating (denoted C-LTO nanosheets), as shown in Fig. 14a and 14b [96]. Afterwards, a self-standing flexible C-LTO nanosheets-based film was fabricated by vacuum-filtration on a Whatman polycarbonate track-etched membrane, which can guarantee interwoven and mechanically robust LTO nanosheet film attached to this membrane (Fig. 14c and 14d). Galvanostatic discharge/charge voltage profiles of C-LTO nanosheets, LTO nanosheets, and nano-LTO electrodes with a wide range from 1C to 100C were also estimated in Fig. 10e. Compared to both LTO nanosheets and nano-LTO electrodes, C-LTO nanosheets electrodes showed an excellent rate performance and a good cycling stability due to the thin uniform carbon layer and the porous structure existed in C-LTO film, which offers more highly conductive pathways for electrons and fast transport channels for Li^+ .

4. Challenges and perspectives

With the rapid development of lightweight, flexible, and wearable electronic devices, flexible and highly efficient energy units are urgently needed. 2D nano-materials introduced in this **article** include graphene paper, graphene composites, and representative **inorganic**-material nanosheets. **A summary regarding flexible electrode based on 2D nanomaterials for Li-ion batteries can be found as well in Table 1.** Although 2D nanomaterials have been widely studied for the

applications in many fields such as supercapacitor, Li-ion battery, catalysis, metal-air battery, Na-ion battery [18,75-77,97-99], its application in flexible energy storage devices, especially flexible Li-ion batteries is still an emerging field. In the case of flexible battery, except for improvement of electro-chemical performance, it is crucial to maintain the excellent stability in terms of electric, capacity, and voltage for these as-prepared flexible batteries under bending. To fulfill these targets, the enhanced adhesion between active materials/flexible current collectors, improved conductivity of the whole flexible electrode as well as optimized design of 2D nanomaterials should be required as well. The main challenges and perspectives in this field include the following aspect:

(1) Most research works have focused on the preparation and characterizations of a single flexible electrode. Preparation of the complete flexible battery in a coherent approach is urgently needed.

(2) More attentions should be paid to develop more efficient and scalable approach to make unique 2D nanomaterial-based electrode and a better matched flexible Li-ion batteries, especially flexible batteries based on new chemistries.

(3) So far, most characterization of 2D nanomaterial-based flexible Li-ion batteries still focus on the battery level performance. Herein, more in-depth studies, including in situ characterization of charge/discharge processes of 2D nanomaterial-based flexible Li-ion batteries are required to further reveal the intrinsic limitation of these batteries and their components, such as active nanomaterials, separator, and current collector under bending.

(4) It is worth noting that three dimensional (3D) integrated electrodes containing 3D conductive network support and active material served for energy storage devices have received increasing attention due to their unique electrochemical superiorities, i.e. great enhancement in

effective contact area between electrolyte/active materials, high efficiency of electron/ion transport and facile diffusion of the electrolyte, and good accommodation of strain induced by the volume change during electrochemical reactions [32,100-103]. In fact, it is possible to make many functional nanosheets deposited onto suitable conductive substrates with three-dimensional structure via in-situ growth or various coating methods to maximize functions of both nanosheets with unique characters, and 3D free-standing films.

(5) Considering emerging serious battery safety concerns, the battery-research mainstream is going back to intrinsic safety issue. Thus, some recent progresses in the all solid-state battery systems, water-phase electrolyte, and solid ion conductors are being gradually disclosed. To smoothly incorporate these aforementioned components into flexible various batteries should be considered as a sweet spot in terms of flexible battery technology and chemistries.

(6) Alternative packaging materials with flexibility, lightness, thinness, stability should be also investigated to protect battery materials, electrolytes and electrochemical reactions from being affected by the external environment.

(7) The assembly technology need to be further investigated. Fabrication of free-standing supports, shape-deformable highly conductive electrolytes, and integration technologies of the full Li-ion battery need to be carefully studied.

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Figure Captions:

Figure 1 An overview of flexible lithium battery electrodes based on 2D graphene paper, 2D graphene/active cathode-material, 2D graphene/active anode-materials, and various 2D inorganic nanosheets/carbon composites.

Figure 2 Schematic illustrations of the laser reduction system with the raster scan path (a), and (b) the flash reduction of graphene oxide whereby a flash from a digital camera reduces graphene oxide. (c) Photograph of the flash-reduced graphene. (d) Scanning electron microscopy (SEM) image of the two characteristic regions of flash-reduced graphene and graphene oxide. (e) The cycling stability measurement of flash-reduced graphene. Reproduced with the permission from Ref. [44].

Figure 3 (a-c) The optical images of as-prepared graphene paper. (d) The SEM image of graphene paper. (e) The discharge/charge curves of flexible graphene paper electrodes. (f) Corresponding rate capability. Reproduced with the permission from Ref. [48].

Figure 4 FESEM images of cross-section (a-c), top-view (d, e) of the graphene/SnO₂ composite paper. (f) The optical image of as-prepared composite paper. (g) The cycling performance of graphene/SnO₂, and bare SnO₂ electrodes. (h) Nyquist plots of graphene/SnO₂, and bare SnO₂ electrodes. Reproduced with the permission from Ref. [52].

Figure 5 (a) Low magnification SEM image of SiNW@G@RGO electrode. The inset: an optical image of a bent SiNW@G@RGO film with excellent flexibility. (b) Cross-section and (c) top-surface SEM images of SiNW@G@RGO electrode. (d) The corresponding region for collecting

EDX spectrum in (e). Reproduced with the permission from Ref. [56].

Figure 6 (a) The TEM image of the as-synthesized LTO/GF composites. (b) TEM image of the LTO nanosheets in LTO/GF. (c) Photograph of a bent LTO/GF//LFP/GF full battery encapsulated by PDMS, showing its good flexibility. (d) Optical image of a flexible Li-ion battery lighting a red LED device. (e) Galvanostatic charging/discharging curves of the battery. (f) Cyclic performance of the battery under flat and bent states. Reproduced with the permission from Ref. [61].

Figure 7 (a, b) The Photographs of a free-standing flexible V_2O_5 /graphene-based battery. (c) Schematic drawing of the flexible Li battery. (d) The rate capability of V_2O_5 /graphene paper and V_2O_5 /Al foil electrodes at different charge/discharge rates. (e) Their corresponding cycling performance at 1C charge-discharge rates. Reproduced with the permission from Ref. [62].

Figure 8 The schematic of the structure and cell operation of TiO_2 nanosheets/graphene (a), and TiO_2 spheres/graphene (b). (c) The optical image of TiO_2 nanosheets/graphene with good flexibility. (d) The corresponding SEM image of TiO_2 nanosheets deposited into graphene. (e) The electrochemical measurements of TiO_2 nanosheets/graphene, and TiO_2 spheres/graphene electrodes. Reproduced with permission. Reproduced with the permission from Ref. [70].

Figure 9 (a) Optical image of free-standing as-fabricated rolled-up TiO_2 (B)/non-woven activated carbon fabric (ACF). (b) Photo of one TiO_2 (B)/ACF composite disc electrode. (c-e) Different magnification FESEM images of TiO_2 (B)/ACF composite electrodes. (f) Charge-

discharge profiles of TiO_2 (B)/ACF composite electrodes for the 1st, 2nd, and 1000th cycles. (g) Cycling performance and Coulombic efficiency of the TiO_2 (B)/ACF electrodes and ACF only electrodes between 1.0-3.0 V at a current density of 335 mA g⁻¹. (h) The rate capability of TiO_2 (B)/ACF electrode, and anatase TiO_2 nanoparticles between 1.0-3.0 V at varied current rates of 1-30 C. (i) Long-term cycling performance and corresponding Coulombic efficiency of the TiO_2 (B)/ACF electrode at 20 C for 2000 cycles. Reproduced with the permission from Ref. [71].

Figure 10 (a) Schematic of the synthesis of CuO nanosheets (NSs)/r-GO paper. (b,c) Cross-section SEM images of the CuO NSs/r-GO composites. Inset: a optical image of an as-prepared free-standing CuO NSs/r-GO electrode, showing its good flexibility. (d) Electrochemical characterizations of CuO NSs/r-GO, bare CuO NSs, and bare r-GO electrodes for Li-ion batteries. Reproduced with the permission from Ref. [72].

Figure 11 (a) Schematic illustration of the fabrication of flexible MoS_2 nanosheets/carbon nanotube paper. (b,c) TEM images of resulting MoS_2 nanosheets/carbon nanotube paper composites. (d) The corresponding EDX mapping. The rate capability performance (e), and cyclic life measurements (f) of MoS_2 nanosheets/carbon tube paper and bulk MoS_2 , respectively. Reproduced with the permission from Ref. [79].

Figure 12 (a) Schematic illustration of the two-step fabrication process of flexible electrodes composed of carbon cloth (CC)-vanadium nitride (VN)/ SnS_2 nanosheets composites. SEM images of (b) the bare CC, (c) VN deposited on the CC, (d) VN/ SnS_2 on the CC. Insets: corresponding optical images of bare CC, CC/VN, CC-VN/ SnS_2 . (e) Cycling performance of

various three electrodes (CC-VN/SnS₂, CC-VN, and CC-SnS₂) at a current density of 0.65 A g⁻¹.

(f) Rate capability of CC-VN/SnS₂, CC-VN, and CC-SnS₂ electrodes at different rates.

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Figure 13 (a, b) The SEM images of 2D ZnMn₂O₄-graphene composite nanosheets and 2D LiFePO₄ nanosheets, respectively. (c) The rate capability of as-synthesized 2D ZnMn₂O₄-graphene composite, and graphite only electrodes. (d) The rate capability of the as-prepared LiFePO₄ nanosheets, and commercial LiFePO₄ powder. Reproduced with the permission from Ref. [87].

Figure 14 (a) The TEM images of the C-LTO nanosheets. (b) HRTEM image of the C-LTO nanosheets, clearly showing some carbon layers incorporated with LTO nanosheets. (c) Optical image of a free-standing highly flexibly C-LTO film. (d) Cross-section SEM image of C-LTO nanosheet film electrode. (e) Galvanostatic discharge/charge voltage profiles of C-LTO nanosheets, LTO nanosheets as well as nano-LTO electrodes cycled at different rates (1C, 5C, 10C, 50C, and 100C). Print with the permission from Ref. [96].

Table

Table 1 Main parameters of 2D nanomaterials-based electrodes for flexible lithium-ion batteries.

nanosheets-based electrode	synthesis method	cycling life	capacity retention	current density	Ref.
Graphene paper	photothermal reduction	1000	156 mAh g ⁻¹	14880 mA g ⁻¹	44
Graphene paper	freeze-drying	100	560 mAh g ⁻¹	100 mA g ⁻¹	48
Graphene/TiO ₂ nanoparticles	filtration	100	157 mAh g ⁻¹	200 mA g ⁻¹	49
Graphene paper/Co ₃ O ₄ fibers	electrostatic interactions	40	840 mAh g ⁻¹	100 mA g ⁻¹	51
Graphene paper/SnO ₂ nanoparticles	filtration	50	438 mAh g ⁻¹	100 mA g ⁻¹	52
Graphene paper/Fe ₃ O ₄ nanoparticles	wet-immersion	100	1427.5 mAh g ⁻¹	1000 mA g ⁻¹	54
RGO/G/Si nanowire	chemical vapor deposition	50	1650 mAh g ⁻¹	840 mA g ⁻¹	56
Graphene/MoO ₃ nanobelts	microwave hydrothermal	100	172 mAh g ⁻¹	100 mA g ⁻¹	63
TiO ₂ nanosheets/graphene	hydrothermal	100	147 mAh g ⁻¹	1680 mA g ⁻¹	70
TiO ₂ nanosheets/activated carbon fabric	hydrothermal	1000	200 mAh g ⁻¹	335 mA g ⁻¹	71
CuO nanosheets/r-GO	hydrothermal	50	736.5 mAh g ⁻¹	67 mA g ⁻¹	72
MoS ₂ nanosheets/carbon nanotube	hydrothermal	100	1091 mAh g ⁻¹	100 mA g ⁻¹	79
SnS ₂ nanosheets/carbon cloth	hydrothermal	100	791 mAh g ⁻¹	650 mA g ⁻¹	80
ZnMn ₂ O ₄ nanosheets/graphene	refluxing	100	734 mAh g ⁻¹	400 mA g ⁻¹	87
MnCo ₂ O ₄ nanosheets/carbon cloth	hydrothermal	60	3 mAh cm ⁻²	800 μ A cm ⁻²	92
Li ₄ Ti ₅ O ₁₂ nanosheets/N-doped carbon	annealing treatment	100	152 mAh g ⁻¹	1750 mA g ⁻¹	96

Figures

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