Laterally Confined Graphene Nanosheets and Graphene/SnO₂ Composites as High-Rate Anode Materials for Lithium-Ion Batteries

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ABSTRACT

High-rate anode materials for lithium-ion batteries are desirable for applications that require high power density. We demonstrate the advantageous rate capability of few-layered graphene nanosheets, with widths of 100–200 nm, over micro-scale graphene nanosheets. Possible reasons for the better performance of the former include their smaller size and better conductivity than the latter. Combination of SnO₂ nanoparticles with graphene was used to further improve the gravimetric capacities of the electrode at high charge–discharge rates. Furthermore, the volumetric capacity of the composites was substantially enhanced compared to pristine graphene due to the higher density of the composites.

KEYWORDS

Carbon, graphene, anode, lithium-ion batteries, SnO₂, nanomaterials

1. Introduction

High-rate performance of lithium-ion batteries is vital to applications that require high power density such as electric/hybrid vehicles and portable power tools, and thus much effort has been devoted to the exploration of high-rate materials [1–3]. It is known that the solid state diffusion of lithium ions in the active electrode materials is the rate-limiting step in most cases [4, 5]. Accordingly, shortening the distance of lithium-ion diffusion is an effective route to improve the rate performance of batteries, which can be realized by fabrication of nanostructured electrodes. For example, nanostructured SnO₂, V₂O₅, and TiO₂ anode

materials manifest better rate capabilities than corresponding thin film or bulk counterparts [6–11].

The rate performance of currently commercial carbonaceous anode materials needs to be improved to generate higher power density, however. It has been demonstrated that small-size graphites exhibit higher capacities than large-size graphites at high charge–discharge rates [12]. Furthermore, the porous structure of carbon nanomaterials, which facilitates the transport of lithium ions in the electrolyte, is crucial for improving the rate performance of the batteries [13–16]. Among the various kinds of carbonaceous anode materials, graphene has newly emerged as one with exceptional properties [17]. The larger interlayer

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distance of few-layered graphene nanosheets compared with graphite leads to graphene having a higher capacity than the theoretical value of graphite ($372 \text{ mA}\cdot\text{h/g}$ [18], corresponding to a stoichiometric composition LiC_6) [17]. The good conductivity and flexibility of graphene nanosheets make them suitable for fabrication into high-performance composites with other anode materials such as SnO_2 and TiO_2 [19, 20]. The width of these graphene nanosheets is usually on the micro scale. It is expected that the performance of the graphene nanosheets would be enhanced if their sizes are reduced, as a result of the shortening of the lithium-ion diffusion path. We have recently synthesized high-purity graphene nanosheets with small size of $\sim 100\text{--}200 \text{ nm}$, so called laterally confined graphene nanosheets [21]. In this article, we demonstrate the exceptional rate capability of this kind of graphene nanosheets. The reversible capacity of the laterally confined graphene nanosheets at high charge–discharge rates is much higher than that of micro-scale graphene. Moreover, the gravimetric and volumetric capacities are both improved by loading SnO_2 nanoparticles on the graphene nanosheets. These results show the great promise of the laterally confined graphene nanosheets and graphene-based composites in lithium-ion batteries with high power density.

2. Experimental

2.1 Material preparation

The laterally confined graphene nanosheets were produced by arc-discharge evaporation of graphite in a $\text{NH}_3\text{--He}$ mixed atmosphere [21]. SnO_2 nanoparticles were loaded onto graphene nanosheets by hydrolysis of SnCl_4 [19]. Typically, NaOH aqueous solution (0.106 mol/L , 50 mL) was added dropwise into an aqueous solution of SnCl_4 (0.054 mol/L , 50 mL) under stirring. The resulting hydrosol was mixed with 200 mg of graphene dispersed in ethylene glycol. After 3 h , several drops of H_2SO_4 (0.1 mol/L) were added to the solution. The precipitate was separated from the solution by centrifugation and heated at 400°C for 2 h in a Ar atmosphere. Micro-scale graphene nanosheets were produced by reduction of graphene oxide in a $\text{H}_2\text{--Ar}$ atmosphere at 800°C for 1 h . The graphene oxide was

obtained by chemical exfoliation of graphite [22].

2.2 Characterization and electrochemical tests

The morphology and structure of the laterally confined graphene nanosheets were examined by scanning electron microscopy (SEM, JEOL JEM-7401) and transmission electron microscopy (TEM, Hitachi H-9000NAR). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2000 diffractometer using $\text{Cu K}\alpha$ radiation. Pore size distributions of the laterally confined graphene nanosheets were obtained from analysis of the desorption branch of the nitrogen sorption isotherms at 77 K (Shimadzu, Micrometrics ASAP 2010) using density functional theory. The content of SnO_2 in the graphene/ SnO_2 composites was determined by thermogravimetric analysis performed on a Q50TGA analyzer (Thermal Analysis Inc.) from room temperature to 900°C at a rate of $10^\circ\text{C}/\text{min}$ under an air flow of $30 \text{ mL}/\text{min}$. Cyclic voltammetry measurements were carried out by using three-electrode cells with lithium metal as the counter and reference electrodes. Galvanostatic measurements were carried out by using two-electrode cells with lithium metal as the counter electrode. The working electrodes were fabricated by compressing the mixture of $90 \text{ wt}\%$ active materials (graphene nanosheets ($1.5 \text{ mg}/\text{cm}^2$) or graphene/ SnO_2 composites ($4.0 \text{ mg}/\text{cm}^2$)) and $10 \text{ wt}\%$ polytetrafluoroethylene onto a copper foil. The working electrodes were dried in vacuum at 120°C for at least 4 h and then assembled as cells in an Ar -filled glovebox (MBRAUN, UNILab, Germany). The electrolyte used was 1.0 mol/L LiPF_6 in a $50:50 (v/v)$ mixture of ethylene carbonate and dimethyl carbonate. Cyclic voltammograms were recorded from 3.0 and 0.05 V at $0.5 \text{ mV}/\text{s}$, by using a Solartron 1280Z electrochemical workstation. The charge–discharge measurements were carried using an Arbin BT-2000 system. Galvanostatic cycling was performed between 3.0 and 0.05 V at various rates to evaluate the rate and cycle performance. All measurements were carried out at room temperature.

3. Results and discussion

Exposed edges of the graphene nanosheets are visible in the SEM image shown in Fig. 1(a). The random arrangement of the nanosheets leads to the formation

Figure 1 (a) SEM and (b) TEM image of the laterally confined graphene nanosheets. (c) High-magnification TEM image showing a five-layered graphene nanosheet

of a porous structure that contains both micropores and mesopores (Fig. S-1 in the Electronic Supplementary Material (ESM)), which should favor the diffusion of lithium ions in the electrolyte to the carbon surface. A TEM image (Fig. 1(b)) shows that the widths of the graphene nanosheets are typically 100–200 nm. Closer inspection revealed that the layer numbers of the nanosheets are mainly in the range from two to six. Figure 1(c) shows a five-layered graphene.

Cyclic voltammetry was employed to study the electrochemical properties of the graphene nanosheets. Figure 2(a) shows the first five cyclic voltammograms of the graphene nanosheets at a rate of 0.5 mV/s in the voltage window 3.0–0.05 V. The reduction and oxidation peaks correspond to the insertion and extraction of lithium ions into/from graphene layers respectively. The remarkable intensity difference between the first and the second reductive sweep indicates a large irreversible capacity, which can be attributed to the decomposition of the electrolyte and the formation of a solid electrolyte interface layer on the carbon surface.

Cycle performance and rate capability of the graphene nanosheets were examined in order to evaluate their potential as anode materials for lithium-ion batteries. The results are shown in Fig. 2(b). The charge–discharge current density was increased stepwise from 65 to 16 000 mA/g and ten cycles were performed at each current density. After the measurements at 16 000 mA/g, the current density was decreased to 65 mA/g in order to test the reversibility and cycle stability. The graphene nanosheets delivered a reversible capacity

of 339 mA·h/g in the first cycle, which is close to the theoretical capacity of graphite (372 mA·h/g). The capacity was not very stable in the first ten cycles where fluctuations in the range 339–319 mA·h/g were observed. When the current density was increased to 550 mA/g, the graphene nanosheets delivered a capacity of 275 mA·h/g, which is 81% of the initial capacity. When the current density was increased to 2500 and 6500 mA/g, capacities of 250 and 184 mA·h/g, respectively, were obtained. Surprisingly, a relatively high capacity of 130 mA·h/g was obtained at 10 000 mA/g, (corresponding to a charge–discharge time of 47 s). A capacity of 32 mA·h/g was retained when the current density was elevated to 16 000 mA/g. To the best of our knowledge, the rate performance of the graphene nanosheets is better than other carbonaceous anodes reported previously [13–16, 23]. Good cyclic performance is confirmed by the fact that relatively stable capacity was obtained at each rate and the capacity after reducing the current density back to 65 mA/g was a little higher than the initial capacity. Figure 2(c) shows the charge–discharge curves of the laterally confined graphene nanosheets at low and high current densities. There is no obvious voltage plateau and the discharging capacity mainly originates in the voltage range 1.5–0.05 V.

For comparison, we also investigated the rate capability of micro-scale graphene obtained from reduction of graphene oxide. Figure 3(a) shows a low-magnification TEM image of the micro-scale graphene. The micro-scale graphene consists of multi-layered nanosheets, as shown by the high-magnification TEM

Figure 2 (a) The first five cyclic voltammograms of the laterally confined graphene nanosheets at a rate of 0.5 mV/s in the voltage window of 3.0–0.05 V. (b) Cycle performance of the laterally confined graphene nanosheets at various charge-discharge current densities. (c) Charge-discharge curves at current densities of 550, 6500, and 16 000 mA/g

image (Fig. 3(b)). The rate performance of the micro-scale graphene is shown in Fig. 3(c). At a low current density of 65 mA/g, the capacity was comparable to that of laterally confined graphene nanosheets. However, at high charge-discharge rates, the capacity was substantially lower than that of laterally confined graphene nanosheets. The capacity of micro-scale graphene nanosheets at 2000 mA/g (68 mA·h/g) was only 27% of that (250 mA·h/g) of laterally confined graphene nanosheets at 2500 mA/g. The charge-discharge curves of the micro-scale graphene nanosheets at current densities of 200 and 400 mA/g are depicted in Fig. 3(d). Similar to the curves for the laterally confined graphene nanosheets, no distinct voltage plateau was observed. Possible reasons for the superior rate capability of the laterally confined graphene nanosheets are their smaller size and better conductivity with respect to the micro-scale counterparts. The length of transport path for lithium ions is shortened in the case of small-size nanosheets and the smaller size leads to a larger solid-electrolyte interface, which facilitates the transport of lithium ions. During the charge-discharge process, lithium ions are inserted/extracted from the open edge of graphene layers. Thus, the presence of more edges in graphene nanosheets leads to higher insertion/extraction rates. Assuming that a square graphene nanosheet with a width of 1 μm is divided into smaller pieces of square nanosheets with widths of 100 nm, the overall length of the edges is increased five-fold. Another factor that may affect the rate capability of the graphene nanosheets is their conductivity. Impedance measurements showed that the conductivity of the laterally confined graphene nanosheets was much better than that of the micro-scale graphene nanosheets (Fig. 3(e)). The lower conductivity of the latter is a consequence of residual oxygenated groups on the graphene. The oxygenated groups cannot be removed completely during the reduction process in a H₂-Ar atmosphere.

The main disadvantage of the carbonaceous anode material is that its capacity is relatively low (theoretical capacity: 372 mA·h/g). A widely used route to circumvent this problem is to combine carbonaceous materials with other high-capacity materials, for

Figure 3 (a) Low-magnification and (b) high-magnification TEM images of micro-scale graphene nanosheets. (c) Cycle performance of micro-scale graphene nanosheets. (d) Charge–discharge curves of micro-scale graphene nanosheets at current densities of 200 and 400 mA/g. (e) Impedance plots of laterally confined and micro-scale graphene nanosheets

example Sn (theoretical capacity: 992 mA·h/g) and SnO₂ (theoretical capacity: 782 mA·h/g [24–27]. In the case of nanostructured high-capacity materials dispersed in a carbon matrix, the latter serves as a buffer to alleviate the strain caused by the volume change of the former during the charge–discharge process. Herein we take graphene/SnO₂ composites as an example to demonstrate the applicability of this route for fabrication of anode materials with high capacity and good rate performance based on laterally confined graphene nanosheets. Adhesion of SnO₂ nanoparticles to graphene nanosheets was confirmed by TEM and XRD. A low-magnification TEM image (Fig. 4(a)) shows SnO₂ particles with diameter of ~4 nm distributed on the surface of the graphene nanosheets. The sample was treated

by sonication in ethanol before TEM observation, so the SnO₂ particles are thought to be strongly anchored on the surface of the graphene. A high-magnification TEM image (Fig. 4(b)) shows that the SnO₂ particles are well crystallized. The XRD pattern of the composites (Fig. 4(c)) reveals a tetragonal rutile-like phase of SnO₂ (JCPDS Card No 41-1445). The content of SnO₂ in the composites was determined to be 67 wt% from thermogravimetric analysis (Fig. S-2 in the ESM). The small size of the SnO₂ particles ensures high-rate insertion/extraction of lithium ions.

Cyclic voltammograms of the graphene/SnO₂ composites at a rate of 0.5 mV/s in a voltage window of 3.0–0.05 V are shown in Fig. 5(a). In contrast with the cyclic voltammograms of the pristine graphene

Figure 4 (a) Low-magnification and (b) high-magnification TEM images of laterally confined graphene/SnO₂ composites. (c) XRD pattern of the composites

nanosheets, some new peaks are observed in Fig. 5(a). It is known that the reaction of SnO₂ involves a two-step process: (1) reduction of SnO₂ to Sn; (2) alloying of Sn with Li to form a series of alloys [28–30]. The new reduction peaks in Fig. 5(a) correspond to the reduction of SnO₂ to Sn and the formation of Li–Sn alloys, while the oxidation peaks correspond to the reverse process.

Figures 5(b) and 5(c), respectively, show the reversible capacities and the charge–discharge curves of the graphene/SnO₂ composites at various current densities. As in the case of pristine graphene, the charge–discharge current density was increased stepwise from 130 to 8000 mA/g. After the measurements at 8000 mA/g, the current density was reduced in order to test the reversibility and cycle performance. As expected, the graphene/SnO₂ composites exhibited higher capacity than the pristine graphene at low current densities. The composite delivered an initial capacity of 673 mA·h/g at 130 mA/g. The capacity was gradually reduced to 513 mA·h/g during the first 10 cycles. The capacities at 450, 1400, 6000, and 8000 mA/g were 424, 295, 190, and 120 mA·h/g, respectively. The cycle and rate performance of the graphene/SnO₂ composites were much better than for pure SnO₂ nanoparticles (Fig. S-3 in the ESM), because the graphene can prevent the large volume change and pulverization of the electrode which occurs in the case of pure SnO₂. When the current density was lowered to 450 mA/g, the composites delivered a capacity of 403 mA·h/g, retaining 93% of the capacity obtained at 450 mA/g in the 20th

cycle. It should be noted that the capacity retention of the graphene/SnO₂ composites was not as good as for the pristine graphene. This may be caused by the aggregation and detachment of SnO₂ nanoparticles to some degree. Although the SnO₂ nanoparticles are dispersed on the surface of the graphene nanosheets, the particles are still able to aggregate during the charge–discharge process. Compared with a SnO₂@carbon core–shell structure, SnO₂ dispersed on graphene in the present study may undergo aggregation and detachment due to the open structure [27].

In order to conveniently compare the rate capability of the laterally confined graphene and graphene/SnO₂ composites, the gravimetric capacities are plotted as a function of charge–discharge rate in Fig. 6(a). The capacity of graphene/SnO₂ composites was substantially higher than that of graphene nanosheets at low current densities. However, the superiority of the composites diminished as the current density increased. Graphene nanosheets exhibited larger capacity than the composite at very rates. We also investigated the rate capability of micro-scale graphene nanosheets loaded with SnO₂ nanoparticles. The micro-graphene/SnO₂ composites exhibited comparable capacities to the laterally confined graphene/SnO₂ composites at 130 mA/g. However, the capacity of the micro-graphene/SnO₂ composites was lower than for the laterally confined graphene/SnO₂ composites at high charge–discharge rates (Fig. S-4 in the ESM). This may be associated with the low capacity of micro-graphene at high rates.

Figure 5 (a) The first five cyclic voltammograms of the laterally confined graphene/SnO₂ composites at a rate of 0.5 mV/s in the voltage window of 3.0–0.05 V. (b) Cycle performance of the graphene/SnO₂ composites at various charge-discharge current densities. (c) Charge-discharge curves at current densities of 450, 6000, and 8000 mA/g

Figure 6 (a) Gravimetric and (b) volumetric capacities of laterally confined graphene and graphene/SnO₂ composites at various current densities

From a practical viewpoint, the volumetric energy density is an important parameter for a battery. In the case of laterally confined graphene nanosheets and graphene/SnO₂ composites used in the present study, the latter has a higher density than the former (1.04 vs. 0.40 g/cm³). Figure 6(b) depicts the volumetric capacities of the two materials at various charge-discharge rates. It is obvious that the volumetric capacities of the graphene/SnO₂ composites are considerably higher than those of the graphene. Therefore,

graphene/SnO₂ composite is a suitable candidate when high rate and small volume are required.

4. Conclusions

Laterally confined graphene nanosheets with size of 100–200 nm exhibit much better rate performance than micro-scale graphene as anode materials in lithium-ion batteries. Capacities of 184 and 130 mA·h/g were obtained at high current densities of 6500 and 10 000 mA/g when using the smaller graphene nanosheets. Loading SnO₂ nanoparticles onto the graphene nanosheets was used to improve the capacity of the anode. The gravimetric and volumetric capacities of the composites were substantially improved compared to pristine graphene. Our study demonstrates that laterally confined graphene nanosheets and graphene-based composites hold a great promise as high-rate anode materials for lithium-ion batteries. Besides SnO₂, the performance of the graphene nanosheets can also be improved by combination with other materials (such as CuO, MnO₂, and Si) to meet the demands for specific applications.

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Electronic Supplementary Material: Supplementary material (pore size distribution of the laterally confined graphene, thermogravimetric trace of the composites of laterally confined graphene and SnO₂, TEM image and cycle performance of SnO₂ nanoparticles and micro-graphene/SnO₂ composites) is available in the online version of this article at <http://dx.doi.org/10.1007/s12274-010-0041-5> and is accessible free of charge.

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