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# Superior cycle stability of graphene nanosheets prepared by freeze-drying process as anodes for lithium-ion batteries

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#### HIGHLIGHTS

• A novel facile synthesis of graphene nanosheets involving freeze-drying technology.

• The as-prepared materials exhibit superior cycle stability and rate performance.

• The freeze-drying helps to enlarge the interlayer distance and specific surface area.

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## ABSTRACT

Graphene nanosheets are synthesized by a novel facile method involving freeze-drying technology and thermal reduction. The microstructure and morphologies are characterized by X-ray diffraction, Brunauer–Emmett–Teller measurements, Fourier transform infrared spectroscopy, and high resolution transmission electron microscope. The results indicate that graphene nanosheets with high specific surface area (358.3 m<sup>2</sup> g<sup>-1</sup>) and increased interlayer distance (0.385 nm) are successfully obtained through the freeze-drying process. The electrochemical performances are evaluated by using coin-type cells versus lithium. A high initial reversible capacity of 1132.9 mAh g<sup>-1</sup> is obtained at a current density of 100 mA g<sup>-1</sup>. More importantly, even after 300 cycles at a high current density of 1000 mA g<sup>-1</sup>, a stable specific capacity of 556.9 mAh g<sup>-1</sup> can be achieved, suggesting the graphene nanosheets exhibit superior cycle stability. The fascinating electrochemical performance could be ascribed to the high specific surface area and the increased layer distance between the graphene nanosheets.

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#### 1. Introduction

Lithium-ion batteries (LIBs) are the most attractive secondary batteries because of their high energy density, relatively low selfdischarge, zero memory effect and excellent safety. Graphene, as a promising anode material for LIBs, has attracted much attention in the recent years due to its superior electronic conductivity, intriguing mechanical properties, and high reversible capacity [1–8]. But graphene still suffers from poor cycling stability and a low specific capacity at high current density, which restricts it from large-scale practical applications. Also graphene nanosheets can easily restack with each other, leading to the loss of the features of graphene [9]. In order to solve the problems, various attempts have been made, such as incorporation of nanotubes or fullerenes [1], design of porous structure [10–14], and introduction of dopants and defects [15–20]. However, most of the above-mentioned modification methods involve complicated and time-consuming production process, which is not economically viable for mass production. Thus, simple, mild and low cost processes are desirable for the preparation of the graphene materials with high electrochemical performance.

Freeze-drying method has been considered to be a simple and efficient approach to retain the microstructure and specific surface area of the treated samples during the drying process. It can be used to create porous structures of nanomaterials [21–24]. In particular, nitrogen and boron co-doped graphene aerogel prepared by freeze-drying technology is applied to the all-solid-state supercapacitors and shows excellent electrochemical performance [25]. This is mainly ascribed to the three-dimensional porous structure with





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high specific surface area formed in the freeze-drying process. In addition, the freeze-drying method is also considered as a promising synthetic way to prepare cathode materials for LIBs [26,27]. Moreover, graphene-based materials obtained through the freezedrying process exhibited excellent rate performance and cycling stability [28–30]. For instance, a SnO<sub>2</sub> nanocrystal/nitrogen-doped reduced graphene oxide nanocomposite prepared and dried by the freeze-drying process demonstrated a reversible capacity of 1346 mAh g<sup>-1</sup> after 500 cycles [30]. However, it is rarely reported that the freeze-drying technology were utilized as a synthetic tool to create nanostructures of graphene materials, especially the lyophilisation effect on structure and physicochemical properties of the graphene materials.

Herein, graphene nanosheets were synthesized by freezingdrying technology followed by thermal reduction. The characterizations and electrochemical performances of the graphene nanosheets obtained by freeze-drying process (denoted as FGNs) and rotary evaporation process (denoted as RGNs) were investigated and compared. The as-prepared FGNs as anode materials for LIBs are expected to show a superior cycle stability and excellent rate performance.

## 2. Experimental section

## 2.1. Synthesis of the FGNs and the RGNs

The FGNs were synthetized by freeze-drying and thermal reduction process from graphite oxides. Graphite oxides were prepared through the modified Hammer's method. Detailed preparation procedure can be found in our previous report [6]. Typically, the as-prepared graphite oxides were dispersed in deionized water by the ultrasound wave to form the graphene oxides. Then, the dispersion graphene oxides aqueous solution was frozen and the ice crystal was sublimated by vacuum freeze-drying. Finally, the as-prepared freeze-dried-material was thermally reduced at 800 °C in argon gas atmosphere and then the FGNs were obtained. For comparison, the RGNs were prepared under the same condition using the rotary evaporation process instead of the freeze-drying process.

#### 2.2. Materials characterization

The morphology and structure of the FGNs and the RGNs were characterized by X-ray diffraction (XRD) patterns from PHI-LIPSPW1710 using Cu/K<sub> $\alpha$ </sub> radiation. The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method (Micromeritics analyzer ASAP 2020 (USA)) at liquid nitrogen temperature. The information of functional groups was measured by Fourier transform infrared spectroscopy instrument (FTIR, Bruker Vector 33). The structure and morphology were characterized by the high resolution transmission electron microscope (HRTEM) (JEM-2010HR).

#### 2.3. Electrochemical measurements

The electrochemical performances were investigated using coin-type half cells. The working electrodes were prepared by coating the slurry of the active materials (80 wt.%), Super P (10 wt.%), and poly(vinylidene fluoride) (PVDF) (10 wt.%) dissolved in an *N*-methyle-2-pyrrolidone (NMP) solvent onto a copper foil and dried in a vacuum oven at 100 °C. Lithium metal was utilized as a counter electrode while the celgard 2325 membrane was used as a separator. The electrolyte was 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in a mixture solution of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 by volume). The CR2025 type coin cells were used as testing batteries

and assembled in an argon-filled glove box where the oxygen and moisture contents were less than 1 ppm.

The cells were galvanostatically discharged and charged using a Battery Testing System (Neware Electronic Co., China) between 0.01 and 3.0 V at different current densities. Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (Zahner IM6ex) over the potential range of 0.01-3.0 V vs. Li/Li<sup>+</sup> at a scanning rate of 0.2 mV s<sup>-1</sup>. Electrochemical impedance spectra (EIS) of the FGNs and RGNs before cycling and after 3 cycles at the current density of 100 mA g<sup>-1</sup> were measured utilizing an electrochemical workstation (Zahner IM6ex). The frequency range was set from 10 mHz to 100 KHz and the potential amplitude was 5 mV.

## 3. Results and discussion

#### 3.1. Materials characterization

XRD patterns of the FGNs and the RGNs are shown in Fig. 1. For FGNs, it is found that a typical weak dispersive and wide (002) diffraction peak at 25.11° is observed, suggests that interlayer distance of nanosheets is large, which is consistent with the previously reported graphene materials [2,3,6]. In strong contrast, the (002) diffraction peak of the RGNs becomes much sharper and more intense, suggesting that the interlayer distance of the graphene nanosheets is serious during the rotary evaporation process [2]. The results indicate that the freeze-drying technology may significantly minimize the restacking of graphene nanosheets.

HRTEM was used to characterize the structure and the interlayer distance of the FGNs and the RGNs. As shown in Fig. 2a, the FGNs are entangled with each other and formed wrinkled paper-like structure. The typical wrinkled structure with corrugation and scrolling is similar to the previous reports [31,32]. Fig. 2b exhibits the interlayer distance between the graphene nanosheets in the HRTEM cross section. The interlayer distance was measured to be 0.385 nm, which is larger than that of graphite (0.335 nm). In order to demonstrate the role of freeze-drying process, HRTEM images of the RGNs were also shown in Fig. 2c and d. It indicates that the graphene nanosheets of the RGNs sample are seriously stacked with each other, which is in agreement with the XRD results. What's more, it is difficult to distinguish the layer distance of the RGNs because of the formation of the stacked graphene nanosheets. The increased layer distance between graphene nanosheets for the FGNs suggests that the interlayer distance is influenced by the



Fig. 1. XRD patterns of the FGNs and the RGNs.

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