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RAPID COMMUNICATION

Graphdiyne for high capacity and long-life lithium storage

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Abstract
There is an increasing demand for improvement of the capacity, rate performance, and life cycle of lithium-ion batteries to meet the requirements of low-emission vehicles, such as hybrid electric and plug-in hybrid electric vehicles. In this article, we report the application of graphdiyne (GDY) as high efficiency lithium storage materials and elucidate the method of lithium storage in multilayer GDY. GDY is a novel carbon allotrope comprising sp- and sp^2-hybridized carbon atoms. Lithium-ion batteries featuring GDY-based electrode exhibit excellent electrochemical performance, including high specific capacities, outstanding rate performances, and a long cycle lives. We obtained reversible capacities of up to 520 mAh/g after 400 cycles at a current density of 500 mA/g. At an even higher current density of 2 A/g, cells incorporating GDY-based electrodes retained a high specific capacity of 420 mAh/g after 1000 cycles.

Introduction

Carbon-based materials are being heavily investigated for their applications as next-generation lithium (Li) storage materials [1-5]. Because of its low cost and high chemical stability, graphite is the most commonly used anode material in commercialized batteries [6]. Nevertheless, its limited Li storage capacity (372 mAh/g, LiC_6) and structural disorder upon prolonged cycling prevent graphite from meeting the increasing demand for Li-ion batteries in the modern world. In the pursuit of higher capacity, rate capability and longer cycling life, other carbon structures have been studied, including fullerenes [7-9], carbon nanotubes (CNTs) [10-13],

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and graphene [14–17]. The carbon atoms in these structures are all sp^2-hybridized, the same as those in graphite. Although the Li capacity can be improved greatly with these different dimensionalities and morphologies, the nature of the Li-intercalated layer does not change significantly when compared to graphite. Graphdiyne (GDY) is a new carbon allotrope that was only synthesized recently [18,19]. GDY is composed of sp^2- and sp-hybridized carbon atoms and is predicted to be the most stable of the various diacetylenic non-natural carbon allotropes. Wang and colleagues confirmed the electronic structure and solid-state structure of GDY determined using X-ray absorption spectroscopy and scanning transmission X-ray microscopy [20].GDY and its unusual structure promises to yield new functional materials displaying novel and enhanced properties. GDY is a 2D, one-atom thick layer of strongly bonded carbon atoms that exhibit chemical stability and electrical conductivity [18,19].Unlike wholly sp^2-hybridized carbon structures, the flat carbon (sp^2 and sp) network endows the GDY material with uniformly distributed pores, and tunable electronic properties. GDY has been predicted to have promising applications as a Li storage material in batteries due to its high capacity and rate capability [20–26]. Here, we are showing that GDY films exhibited a high specific Li capacity, long cycle life, and high stability as electrode materials in Li-ion batteries. The reversible capacities of GDY films are up to 520 mAh/g after 400 cycles at a current density of 500 mA/g and the cells incorporating GDY-based electrodes retained a high specific capacity of 420 mAh/g after 1000 cycles at an even higher current density of 2 A/g.

The structure of GDY is related to that of graphene, but with the introduction of butadiynelinkages ($-C\equiv C-C\equiv C-$) to form 18-C hexagons (Fig. 1). With regard to applications in Li storage, many theoretical studies, using density functional theory [24] and first-principles calculations [21,25], have determined the absorption and diffusion of Li atoms within GDY. High-capacity Li storage in the form of LiC_3 (744 mAh/g) has been predicted—twice the specific capacity of graphite. The unique atomic arrangement and electronic structure of GDY enable Li atoms to diffuse readily upon a GDY layer with moderate energy barriers ranging from 0.18 to 0.84 eV. Compared with graphene, the 18-C hexagon structure of GDY results in a lower atom density and, accordingly, a larger specific surface area. Taken together, all of these features suggest that GDY has the potential to ensure efficient Li storage.

In this study, we demonstrate the application of GDY as an efficient Li storage material for the fabrication of high-performance Li-ion batteries. We achieved a battery exhibiting high specific capacity, an outstanding rate performance, and a superior cycle life through the direct use of GDY fabricated on a copper surface without the addition of any polymer binders or conductive additives. This battery featured a reversible capacity of up to 520 mAh/g after 400 cycles at a current density of 500 mA/g. At an even higher current density of 2 A/g, cells incorporating GDY-based electrodes retained their high specific capacity at 420 mAh/g after 1000 cycles. We elucidate the method behind the Li atom storage in multilayer GDY by using GDY with varying thicknesses. The intercalation of Li atoms occurs primarily through both interlayer insertion/extraction process and surface absorption/desorption process.

Experimental section

Synthesis of GDY films

Copper foil was washed with 4 M hydrochloric acid (HCl) (100 mL), sonicated for 3 min, washed with water and ethanol, sonicated for 3 min, washed twice with acetone, and dried under nitrogen (N_2). Several (10) pieces of copper foil ($2 \times 2\ cm^2$) and pyridine (50 mL) were charged in a three-neck flask; the mixture was heated at 120 °C under N_2 for 1 h and then the temperature was decreased to 80 °C. Hexakis[(trimethylsilyl)ethynyl]benzene (50 mg) was dissolved in tetrahydrofuran (THF) (50 mL) in an ice bath (ice and ammonium

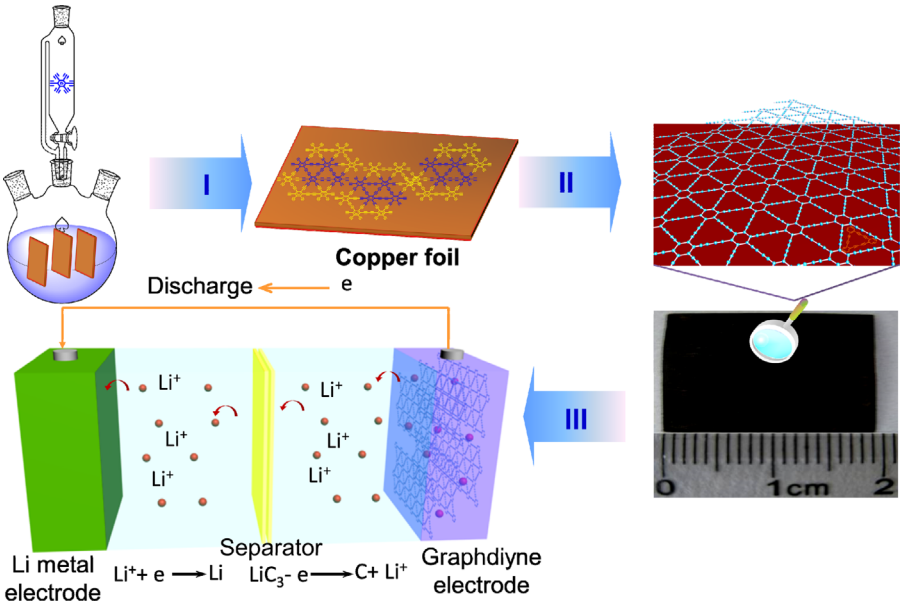

Fig. 1 Schematic of the GDY synthesis and Li-ion batteries preparation process. (I) synthesis schematic of GDY. (II) photograph of GDY sample and Ball-and-stick model of the structure of GDY. (III) representation of an assembled GDY-based battery.