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Research paper

Graphdiyne Nanowalls as Anode for Lithium—Ion Batteries and Capacitors Exhibit Superior Cyclic Stability

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ABSTRACT

In this study, we reported the design and application of hierarchical porous Graphdiyne Nanowall (GDY—NW) for energy storage device as lithium—ion batteries (LIBs) and capacitors (LICs). The unique hierarchical porous with the presence of butadiyne linkages comprising *sp*— and sp^{2-} hybridized carbon atoms reinforces not only providing rich active sites for lithium storage, but also the efficient pathways for fast ion diffusion. Future more, the stable SEI layer formed on the GDY—NW surface after the initial cycle which can effectively reduce the resistance of interface and thus stable the circulating batteries, confirmed directly through the in—situ Raman measurement. The GDY—NW electrodes exhibit a reversible capacity of approximately 908 mAh g^{-1} at 0.05A g^{-1}, excellent cyclic stability with retention of 526 mAh g^{-1} at large rate of 1 A g^{-1} after 1000 cycles applied as anode for LIBs. Thus GDY—NW films could deliver a capacitance more than 189 F g^{-1} over 10000 cycles at 1 A g^{-1} for LICs with active carbon cathode and exhibit an initial specific energy as high as 217 Wh kg^{-1} at a power density of 100W kg^{-1}, presenting the benefit of the unique hierarchical porous structure comprising amount of macro, meso— and micro—pores, for thus high performance capability and cyclicity for renewable energy lithium storage.

1. Introduction

The development of renewable energy (such as solar energy, wind power, hydropower, and geothermal energy) is becoming a high priority. In the meantime, storage of renewable energy needs to be improved with high energy and power densities simultaneously with superior cycle life and low cost due to their limited charge storage capability, energy conversion efficiency and rate [1,2]. Lithium ion batteries (LIBs) have been one of the most used power supplies for small electronic devices since 1990s, because its relative high energy and power density compared with lead-acid batteries or nickel-metal hydride batteries [3,4]. However, for the rapid advancement of electronic and the increasing demand for large—scale energy storage such as electric vehicle or power walls, advanced LIBs with high energy density, high power density, and better cyclic stability are needed [5–7]. In a typical LIB device, reactions are accompanied with both lithium ion and charge transfer through the electrodes as well as dimension change along with the structure damage of the active materials leading to poor cycle ability. In addition, the contact interface and the transport distance of the electrode material critically determine the performance of the LIBs in practice. There have been many novel approaches to gain high energy storage capacities and charge—discharge rates without sacrificing the cyclicity. Nanostructured electrodes are seemingly the most promising solution for future advanced lithium ion batteries [8]. The application of ingenious constructed nanostructures, multi-point active interfaces and hierarchical porous structure has also promoted the fabrication of electrodes directly without binders and conductive additives which are typically used in the fabrication of advanced lithium ion battery electrodes, simplifying the electrode fabrication process and enhancing electrode storage density. Accordingly, multivalent transition metal oxides/sulfides/hydroxides compounds (such as Co_3O_4, MnO_2, NiO, et al) offer high theoretical capacity for lithium ion storage and apply to anode materials in LIBs energy systems with simply preparation of hierarchical porous structure including nanowalls, nanoclusters, and nanoparticles [9–11].However, transition metal compound nanostructures generally suffer from poor conductivity and instability in electrochemical process. The irreversible phase transition specifically at high lithiation/delithiation rates, leading to poor rate cycle performance and seriously limited the

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lifetime of LIB batteries [12,13]. Recently, nanostructured carbonaceous materials (for example: graphene, carbon nanotubes, carbon nanofiber, and so on) have received intensive interests in lithium storage and conversion applications due to their ingenious constructed nanostructures, high conductive and nanoporous structure [14,15]. Nevertheless, pristine carbon nanomaterial is difficulty to further improve the electrochemical activities and ion transport channel such as enough pores and defects [16]. To create hierarchical porosity, chemical activation, hydrothermal reaction and calcination constantly apply to carbonaceous nanomaterials to enrich a three–dimensional (3D) hierarchical porous and defects to enhance the lithium storage activity sites and fast lithium diffusion [17–19]. However, from a practical point of view, it is also not efficient and yield for fast production of carbonaceous nanomaterial. Lithium-ion capacitor (LIC), a novel energy storage device generally combining the LIB anode material and electrochemical double-layer capacitor (EDLC) cathode material, has featuring the best characteristics of both LIB and EDLC such as higher power density and longer cycle life than LIBs and a higher energy density than EDLC. During the charge–discharge process, anion adsorption/desorption on the activated material occurs on the cathode of typically LICs, whereas, lithium ion intercalation/de-intercalation occurs within the anode electrode. Therefore, the electrochemical performance of LIC is usually limited by the anode electrode since intercalation/de-intercalation reaction of lithium ion is much slower. Study on the novel anode material is the key factor to improve the performance of LICs [20,21].

Graphdiyne, a novel carbon–rich materials discovered recently, contains numerous large triangle–like pores that can form a unique Li triangular occupation pattern to promote the alternating distribution of Li atoms on both sides of GDY molecular plane. [22–24] Therefore, the Li storage capacity of GDY monolayers could be predicted to reach as high as LiC_3, 2 times than the Li storage capacity of graphite as LiC_6. [25,26] In our previous study, we also reported that bulk GDY exhibited high specific capacity, excellent rate performance and long cycle life as anode materials both in application of lithium ion batteries and capacitors (LIBs and LICs) [27–29]. To further optimize the Li storage performance of thus GDY materials, it is significant to enhance the hierarchical porosity structure between the GDY monolayers and GDY sheets to rich more active sites and enhance the efficient pathways for fast ion diffusion. Herein, Liu et al. reported the syntheses of graphdiyne nanowalls (GDY–NW) through a modified Glaser–Hay coupling reaction to control the growth of porous nanostructure of GDY sheets [30]. It is reasonable to consider that the unique hierarchical nanostructure of GDY is able to improve the rapidly transportation, the migration and diffusion of Li ions from GDY monolayers to GDY sheets and 3D GDY nanostructure network, respectively [31–33]. Meanwhile, GDY with abundant hierarchical porous nanostructure is supposed to improve the cycle stability during the less irreversible phase transition at high lithiation/delithiation rates, leading to better rate and cycle performance in a stable and homogeneous solid interface. The bulk GDY had been applied for electrochemical double layer capacitors (EDLCs) delivered a specific capacitance of about 71.4 F g^{-1} from at a constant discharge current density of 3.5 A/g [34]. However, such results need to be further improved. Thus, we designed a novel anode based on self–assembled GDY nanowall (NW) and applied this anode in LIBs and LICs. The results reveal that the LIBs with GDY–NW electrodes exhibited a higher capacity of approximately 908 mAh g^{-1} at 0.05 A g^{-1}, and excellent cyclic stability with retention of 526 mAh g^{-1} over 1000 cycles at large rate of 1 A g^{-1}. The formation of stable SEI layer was observed through the *in–situ* Raman measurement and revealed that it could effectively reduce the resistance of interface and thus stable the circulating batteries after the initial cycle. Especially, the fabricated GDY–NW based LICs deliver a special capacitance approximately 189 F g^{-1} over 10000 cycles at 1 A g^{-1}, and exhibit a high energy density of 217 Wh kg^{-1} at specific power of 100 W kg^{-1}. Such results further confirmed the benefit of the hierarchical porous nanostructure of GDY for lithium storage with high capability and cycle stability. This study also suggested that the obtained GDY–NW could be a potential competitor for application in high performance Li rechargeable batteries.

2. Experimental

2.1. Preparation of GDY–NW

GDY–NW was prepared as reference via a modified Glaser–Hay coupling reaction as shown in Fig. 1 [30]. The precursor [Hexakis [(trimethylsilyl)ethynyl] benzene (HEB–TMS)] was obtained following the reported synthetic route [23]. The HEB monomer could be obtained after deprotection of HEB–TMS by tetrabutylammonium fluoride (TBAF) and used immediately. Cu foil was used as reaction substrate and copper ion source. Before the preparation of GDY–NW, Cu foil was carefully dipped in 1 M hydrochloric acid solution more than 24 hour, and then washed with distilled water and ethanol and acetone several times under argon atmosphere. Several (more than 10) pieces of copper foil (2 × 20 cm) were added to the mixed solution of acetone, pyridine and tetramethylethylenediamine (TMEDA) with a volume radio of 100:5:1 in a flask. 10 mg HEB was dissolved with 50 ml acetone and added into the mixed solution under strict water–free and oxygen–free conditions. Then the mixture was kept at 50 °C for 12 hours. GDY–NWs were grown on the surface of copper foil during the reaction. Finally the copper substrate were washed with heated acetone and ethanol several times and dried under nitrogen. The average mass loading of GDY-NW active materials at a range of 0.13–0.08 mg/cm^2 (with different reaction condition) was calculated by completely dissolved a certain area of GDY-NW contained cooper foli in 6 M hydrochloric acid solution with a small amount of ammonium persulfate to dissolve copper gradually, the exfoliated

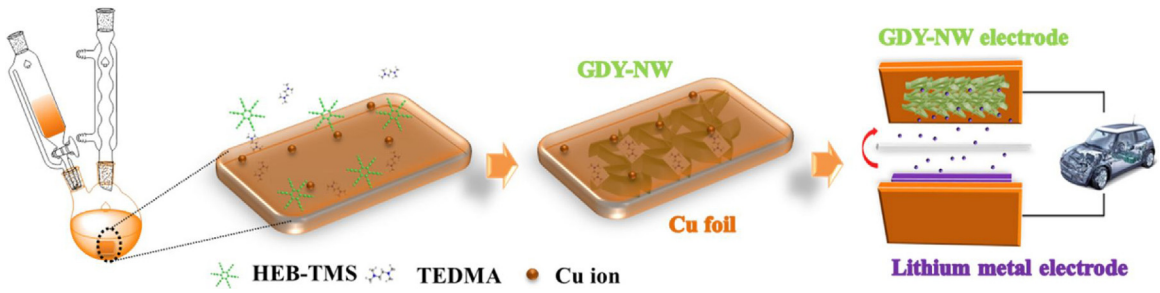

Fig. 1. Schematic of synthesis of GDY–NWs and LIB based on GDY–NW.