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Reduced graphene oxide/carbon nanotubes sponge: A new high capacity and long life anode material for sodium-ion batteries



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HIGHLIGHTS

- Graphene/carbon nanotubes sponge was fabricated via a simple freeze drying method.
- The hybrid sponge was employed as anode materials of sodium ion batteries.
- The hybrid sponge exhibits high capacity and superior long life cycling stability.

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ABSTRACT

Reduced graphene oxide/carbon nanotubes (CNTs) sponge (GCNTS) is fabricated via a simple freeze drying of graphene oxide/CNTs mixed solution and subsequent thermal treatment in nitrogen atmosphere, and used as anodes for sodium-ion batteries (SIBs) for the first time. The morphology, structure and electrochemical performance of GCNTS are characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, nitrogen adsorption-desorption isotherms, galvanostatic charge/discharge tests, cyclic voltammetry and electrochemical impedance spectroscopy, respectively. The results show that GCNTS with 20 wt % CNTs has a highest charge capacity of 436 mA h g⁻¹ after 100 cycles at a current density of 50 mA g⁻¹ and even at a high current density of 10 A g⁻¹, a capacity of 195 mA h g⁻¹ is maintained after 7440 cycles. The high capacity, excellent rate performance and long life cycling enable the GCNTS to be a promising candidate for practical SIBs.

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1. Introduction

Nowadays, the dominance of lithium-ion batteries (LIBs) is obvious in a wide range of applications such as cellular phones, laptops, full and hybrid electric vehicles [1–9]. The successful commercialization of LIBs owes to their outstanding energy density, fast charge-discharge rate, long lifespan, light weight and environmental friendliness [1–9]. However, driven by the large-scale applications of LIBs, the limited lithium sources and relatively high cost hinder their further development and applications [10–13]. As such, this creates a need to develop new high

performance battery systems beyond LIBs [10–13]. Sodium-ion batteries (SIBs) have attracted recent attention for application in large-scale energy storage due to abundant sodium resources, low cost and similar chemical properties between sodium and lithium [11–13]. However, a major challenge in developing SIBs is in obtaining suitable electrode materials which are capable of hosting large sodium ion (1.02 Å) with sufficient capacity, highly reversible sodiation-desodiation and long life cycling [11–13].

Carbon-based materials are thought as an attractive candidate for SIBs anode due to their stable physicochemical property, excellent electrical conductivity, abundant resource and low cost [14]. In the last decades, carbon-based materials, including nitrogen-doped carbon microspheres (a capacity of 336 mA h g⁻¹ after 50 cycles at 50 mA g⁻¹) [15], hollow carbon nanospheres (a capacity of 260 mA h g⁻¹ after 100 cycles at 90 mA g⁻¹) [16], carbon nanowires (a capacity of 200 mA h g⁻¹ after 200 cycles at 125 mA g⁻¹) [17], carbon nanobubbles (a capacity of 150 mA h g⁻¹

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after 80 cycles at 100 mA g^{-1} [18], carbon fiber (a capacity of 247 mA h g^{-1} after 200 cycles at 100 mA g^{-1}) [19], and porous carbon/reduced graphene oxide (rGO) composite (a capacity of 400 mA h g^{-1} after 100 cycles at 50 mA g^{-1}) [20] were employed as anode materials for SIBs, and showed excellent electrochemical performance. To date, despite such encouraging progress, the performance combination of high reversible capacity, excellent rate performance and long-term cycling stability has seldom been reported for carbon anodes, and thus further work to improve their electrochemical performances is still necessary to meet the practical application for SIBs. Among various carbon species, graphene with a flexible planar single sheet of carbon atom structure, strong chemical durability, outstanding specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), excellent thermal conductivity (5000 W m K^{-1}) and high electrical conductivity ($7.2 \times 10^5 \text{ S cm}^{-1}$) is a potential candidate for SIBs [21]. However, it has been found that the strong π - π interactions between graphene sheets may cause the problems of poor dispersion, restacking and multilayer thickness of graphene sheets during the preparation process, which prevent the full realization of its high specific surface area, excellent electrical conductivity and high theoretical capacity, resulting in the unsatisfied electrochemical performance for SIBs (a capacity of 150 mA h g^{-1} after 50 cycles at 100 mA g^{-1}) [22,23].

Designing a novel structure of graphene, such as 3-dimensional (3D) rGO architectures, is an effective method to solve the above problem [24]. These re-designed rGO structures usually possess interconnected macropores that buffer ions to shorten the diffusion distance from the electrolyte to the interior surface. Various 3D rGO materials have been reported with excellent electrical conductivity, high specific surface area and good mechanical properties with wide applications in solar cells [25], supercapacitors [26], fuel cells [27], capacitive deionization [28] and LIBs [29]. However, the use of these 3D rGO for SIBs has not been investigated in detail, with only Dai's group synthesizing nitrogen-doped rGO foams using a freeze drying method and subsequent thermal treatment in NH_3 . The foams showed a high charge capacity of about 594 mA h g^{-1} after 150 cycles at a current density of 500 mA g^{-1} for SIBs [30]. However, the cycling stability during long-term cycling, in particular at high current density, which is critical for practical application, was not studied in their work. It is a well known fact that graphene sheets can adhere and stack to graphite platelets between macropores, hampering the electrolyte ions from accessing the inner layers within 3D rGO architectures.

Currently, another effective strategy to alleviate the inevitable aggregation of graphene sheets is to combine rGO with some guest materials (e.g. pyridine, activated carbon and carbon nanotubes (CNTs) et al.) [25,31]. Amongst them, CNTs exhibit excellent electrical properties, good mechanical and chemical stability, which have been widely used in combination with rGO for supercapacitor [32] and LIBs [33]. Researchers have reported that rGO/CNTs composites showed considerably improved performance, especially better cycling stability compared with the pristine rGO [32,33]. Such rGO/CNTs composites should be expected to exhibit excellent electrochemical performance as anode of SIBs. However, the application of rGO/CNTs, especially 3D rGO/CNTs sponge (GCNTS) in SIBs has not been reported to date. In this work, GCNTS was used as anode of SIBs for the first time, and exhibits high capacity, good rate capability and especially excellent cycling stability even at high current density.

2. Experimental

2.1. Synthesis

Graphene oxide (GO) was obtained from commercial graphite

by a modified Hummers method, which has been reported in our previous work [28]. For the synthesis of rGO sponge (GS) and GCNTS, in a typical process, CNTs (Nanotech Port Co. Ltd, Shenzhen, China) aqueous dispersion was added into a vial containing GO aqueous dispersion. In this step, the weight ratio of GO to CNTs was changed by adjusting the volumes of GO solution and CNTs solution. The mixed solution was stirred under magnetic stirring, and then the vial was placed into a freezer. After the mixed solution was frozen, the vial was moved to a freeze-dryer ($-53 \text{ }^\circ\text{C}$, pressure $< 10 \text{ Pa}$) for 3 days to obtain the GCNTS. Finally, GCNTS was calcined at $800 \text{ }^\circ\text{C}$ for 3 h in nitrogen atmosphere. GS was also prepared for comparison according to similar procedure without the use of CNTs.

2.2. Characterization

The morphology of the samples was characterized by field-emission scanning electron microscopy (FESEM, JSM-7001F, JEOL) and transmittance electron microscopy (TEM, JEM-2010, JEOL). The X-ray photoelectron spectroscopy analysis (XPS) was carried out on Kratos Axis Ultra using a monochromatic Al $K\alpha$ radiation. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 449F3 simultaneous thermogravimetric analyzer in nitrogen with a temperature range from 30 to $800 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The crystalline phase of the samples was characterized by X-ray diffraction (XRD, DX-2700, Fangyuan) measurement using Cu $K\alpha$ radiation with $\lambda = 1.54145 \text{ \AA}$. Raman spectra were recorded on a Raman Spectrometer (RM-1000, Renishaw) with 632.8 nm He-Ne lasers as irradiation source. The bulk electrical conductivities of the samples were measured using a DDSJ-308A Conductivity Meter through a four-probe method with metal electrodes attached to the ends of the samples. The pore size distribution and Brunauer-Emmett-Teller (BET) specific surface area were deduced from the nitrogen physical adsorption measurement data obtained using an ASAP 2010 Accelerated Surface Area and Porosimetry System (Micromeritics, Norcross, GA), and the pore size distribution was derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model.

2.3. Electrochemical measurement

For electrochemical testing, the samples, Super-P carbon black and polyvinylidene fluoride were mixed in N-methylpyrrolidone solvent with weight ratio of 80:10:10 to form a homogenous slurry and coated on a copper foil followed by drying at $120 \text{ }^\circ\text{C}$ overnight in vacuum oven. Coin type cells (CR2032) were assembled in a glove box (MB-10-compact, MBRAUN) under Ar atmosphere, with oxygen and water contents less than 0.5 ppm , where sodium metal foil and Whatman glass fiber membrane were used as the counter electrode and separator, respectively. The electrolyte was 1 M NaClO_4 solution in ethylene carbonate and propylene carbonate (1:1, w/w). Galvanostatic charge-discharge test was conducted on a LAND2001A battery test system in a voltage range of 0.005 – 3 V at a current density of 50 mA g^{-1} unless otherwise specified. Cyclic voltammetry (CV) was performed using an electrochemical workstation (AUTOLAB PGSTAT302N) in a voltage range of 0.005 – 3 V at a scan rate of 0.5 mV s^{-1} at room temperature. Electrochemical impedance spectroscopy (EIS) measurement was carried out on the same electrochemical workstation in a frequency range of 0.01 Hz – 100 kHz , and the applied bias voltage and ac amplitude were set at the open circuit voltage of the cells and 5 mV , respectively.

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