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Design of $Fe_{3-x}O_4$ raspberry decorated graphene nanocomposites with high performances in lithium-ion battery☆

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ABSTRACT

$Fe_{3-x}O_4$ raspberry shaped nanostructures/graphene nanocomposites were synthesized by a one-step polyol-solvothermal method to be tested as electrode materials for Li-ion battery (LIB). Indeed, $Fe_{3-x}O_4$ raspberry shaped nanostructures consist of original oriented aggregates of $Fe_{3-x}O_4$ magnetite nanocrystals, ensuring a low oxidation state of magnetite and a hollow and porous structure, which has been easily combined with graphene sheets. The resulting nanocomposite powder displays a very homogeneous spatial distribution of $Fe_{3-x}O_4$ nanostructures at the surface of the graphene sheets. These original nanostructures and their strong interaction with the graphene sheets resulted in very small capacity fading upon Li^+ ion intercalation. Reversible capacity, as high as 660 mAh/g, makes this material promising for anode in Li-ion batteries application.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronic devices, and show increasing interest for powering electric vehicles [1]. To date, most of commercial LIBs use graphite as negative electrode thanks to its low discharge plateau and cycling stability [1–4]. However, graphite specific capacity is limited to 372 mAh/g upon Li^+ intercalation, and exhibits poor rate performance associated with the risk of metallic Li deposition at high charging regimes [1,5]. To meet the demand in high energy and high power electrochemical storage devices, alternative anode materials have been investigated [6,7], including alloying reaction metals [8], or conversion reaction oxides [9–11]. Among them, spinel iron oxide Fe_3O_4 has been considered as a promising oxide thanks to its high theoretical capacity of 924 mAh/g, its environmental benign, large abundance and low cost [5,6,9,12–16]. Moreover, Fe_3O_4 shows a potential around 1 V versus Li^+/Li, which provides better safety versus metallic Li deposition at high rate. However these applications are limited by poor cycling performance arising from the structure breakdown linked with volume change during the electrochemical reaction with Li, as well as important polarization during the charge/discharge processes [5,15,17,18]. To increase the number of cycles, various approaches have been proposed such as carbon based coating [15,19], electrodes nanostructuring [11,16,17,20], or nanocomposites [5,18,21]. Taberna et al. proposed to attach Fe_3O_4 nanoparticules onto nanostructured copper foil by electrodeposition [11] but the best performances were obtained using carbon-based composites such as carbon shells, carbon nanotubes, or graphene [16,22–24]. Besides, $Fe_{3-x}O_4$ nanostructures, consisting of aggregates of nanocrystals, have shown interesting performances as electrode material [25,26] but the low electronic conductivity of iron oxide leads to poor rate performance and they require thus the addition of non-electroactive material such as acetylene black.

Graphene and few-layer graphene (FLG) materials have received an ever increasing scientific interest during the last decades thanks

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to their exceptional physical properties [27–30]. These 2D materials can be synthesized by different methods such as micromechanical alleviation of graphite, liquid-phase exfoliation, mechanical ablation, high-temperature treatment of silicon carbide, catalytic or chemical unzipping of carbon nanotubes as well as chemical vapor deposition (CVD) or by reduction of graphene oxide (GO) [31–36]. In the LIB application, it is expected that graphene and FLG could play a significant role to stabilize deposited transition metal oxides, improving the electrical conductivity of the composite and voids for accommodating volume change during the charge/discharge cycles.

We recently synthesized nanohybrid materials combining metal oxide nanoparticles (M = Co or Fe) with an extremely narrow size distribution and carbon nanotubes [37,38] or few-layer graphene (FLG) [39] with a metal oxide content up to 50%. Iron oxide nanoparticles with mean diameter ranged from 5 to 50 nm (depending on the synthesis conditions) were well dispersed on both side of the FLG surface, according to the recent TEM tomography analysis [40]. These nanoparticles further act as spacers to prevent the complete restacking of the FLG through van der Walls forces.

Using a similar approach, porous $Fe_{3-x}O_4$ hollow nanostructures with a raspberry shape, narrow size distribution, well-defined chemical composition and crystalline structure [30] were successfully grown onto few-layer graphene sheets with highly controlled covering density. These nanostructures consist of oriented aggregates of magnetite nanocrystals (nanocrystals with common crystallographic orientations directly combined together to form larger ones) which ensure a nanostructuration, porosity and a low oxidation state of Fe_3O_4 nanocrystals [41]. The structure of such a composite presents several interests for electrode material such as (i) a high porosity that provides both high electrode/electrolyte interface area and fast Li^+ diffusion path toward active reaction sites, (ii) a preservation of the magnetite composition at low nanocrystal sizes (as described in ref. [30]) that improves the capacity performance, and (iii) a highly conductive graphene matrix that provides an excellent interface with the $Fe_{3-x}O_4$ nanostructures and ensures high electronic percolation without the need of conducting additives, and (iv) the strong interaction between the iron oxide and the graphene surface which significantly reduces the problem of deactivation linked with the excessive sintering of the iron oxide compounds upon LIB experiments. The 2D morphology of the FLG also contributes to the flexibility of the composite as a function of charge/discharge cycle and to prevent the breaking of the composite structure for long-term operation.

In this work, we report on the use of these $Fe_{3-x}O_4$ raspberry shaped nanostructures deposited on graphene sheets (synthesized by an "ultimate" exfoliation of expanded graphite), as anode material for LIB application. The composite demonstrates specific capacity values as high as 660 mAh/g at 8 C with excellent cycling stability. The samples, before and after LIB tests, were also characterized by different techniques in order to get more insight about the possible structural modification during the charge/discharge cycling and also for subsequence optimization process.

2. Experimental

2.1. Graphene and few-layer graphene synthesis

Few-layer graphene (FLG) powders were obtained using a technique derived from the synthesis developed by Janowska et al. based on an "ultimate" exfoliation of graphite-based material or expanded graphite [42,43]. The expanded graphite powder Carbon Lorraine was dispersed in ethanol by an ultrasonic treatment (finger) during 30 min: ultrasonic finger is a "Branson" instrument (Digital sonifier 450) with a maximal power of 400 W (in reality 20% to 40% of the maximal power was used). After the solution containing the powder was decanted for 1 h, the supernatant solution containing the smaller particles was collected and the operation was repeated two times to obtain the few-layer graphene powder.

2.2. Synthesis of $Fe_{3-x}O_4$@graphene hybrid nanostructure

The $Fe_{3-x}O_4$@graphene was synthesized by a one-step mixed polyol-solvothermal method. In a typical synthesis, iron chloride hexahydrate (1.00 mmol), succinic acid (0.33 mmol), urea (10.0 mmol) and a given amount of graphene (10.0 mg, 20.0 mg and 100.0 mg) were dispersed in ethylene glycol (10.0 mL) by vigorous mechanical stirring and ultrasonication. The solution was subsequently sealed in a Teflon lined stainless steel autoclave (20 mL volume), slowly heated at 200 °C for 4 h and maintained at this temperature for 10 h. After cooling down to room temperature, the precipitated powder was separated by centrifugation and was then washed several times using deionized water and ethanol. Finally, the powder was freeze dried before characterizations. Samples were named NC-10, NC-20 and NC-100 accordingly to the amount of graphene used.

2.3. Structural characterizations

Scanning electron microscopy (SEM) analysis was carried out on a JEOL 6700F microscope working at 10 kV accelerated voltage. Transmission electron microscopy (TEM) was carried out using a JEOL 2100F (voltage 200 kV) microscope with a point resolution of 0.2 nm. The sample was dispersed in ethanol by ultrasonication during 5 min and a drop of the solution was then deposited on a copper grid (covered with a carbon membrane). X-ray diffraction (XRD) was carried out using a Bruker D8 Advance in the 27°–75° (2θ) range with a scan step of 0.03°. The detector was a three degrees wide analysis detector ("Lynx Eye"). Thermal gravimetric analyses were carried out with a TA Instrument (Q-5000 model). They were performed under an air flow (20 mL/min) up to 1000 °C with a heating rate of 5 °C/min. The specific surface area was determined with a Micromeritics sorptometer (Tristar). The sample was outgassed at 250 °C under vacuum for 12 h in order to desorb moisture and adsorbed species on its surface. The measurements were carried out using N_2 as adsorbent at liquid N_2 temperature.

2.4. Electrochemical characterizations

2-electrode Swagelok cells were assembled in an argon-filled glove box using the nanocomposite powder as the positive electrode and the Li metal as the negative electrode. A Whatman GF/B borosilicate glass-fiber (520 μm-thick) saturated with 1 M $LiPF_6$ electrolyte solution (in EC : DMC=1 : 1 in volume ratio) was used as the separator. Powders were used without any conducting additives. The electrode loading was between 2 and 2.5 mg/cm^2. All measurements were carried out using a Bio-Logic WMP 3 potentiostat, between 0.05 and 3 V (versus Li/Li^+). The rate performance was obtained by the so-called “signature” experiment as described in details in the reference [11].

3. Results and discussions

Fig. 1(a–d) shows SEM images of the graphene/$Fe_{3-x}O_4$ nanocomposites with three different weight ratios raspberry $Fe_{3-x}O_4$ nanostructures/graphene (1 for NC-100, 5 for NC-20 and 10 for NC-10). The mean $Fe_{3-x}O_4$ nanostructure size is centered to 250 nm and is very similar for all three samples meaning that the amount of graphene does not affect the formation of iron oxide nanostructures. They consist of original orientated aggregates of $Fe_{3-x}O_4$ nanocrystals (Fig. 1e) with a mean size of 25 nm, mainly