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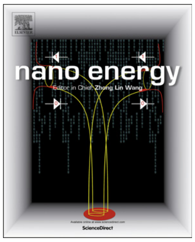

RAPID COMMUNICATION

Co_3O_4/nitrogen modified graphene electrode as Li-ion battery anode with high reversible capacity and improved initial cycle performance

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Abstract
Co_3O_4 nanoparticles are grown on nitrogen modified microwave exfoliated graphite oxide (NMEG) with weight ratio controlled from 10% to 70%. Electrochemical performance reveals that the obtained Co_3O_4/NMEG composite as Li-ion battery anode exhibits improved cycle stability, excellent reversible capacity, high current rate performance, and reduced irreversible capacity loss in the initial cycle compared to pure Co_3O_4 without graphene or Co_3O_4 on thermally reduced graphene oxide (tRG-O). The 70%Co_3O_4/NMEG composite has initial irreversible capacity of 230 mAh g^{-1} (first cycle efficiency of 77%), and 910 mAh g^{-1} of capacity is retained after 100 cycles. The 70%Co_3O_4/tRG-O delivers a reversible capacity of 750 ± 20 mAh g^{-1}, and the irreversible capacity loss during the first cycle is 700 ± 20 mAh g^{-1}. Nitrogen functional groups in NMEG, especially pyridinic and pyrrolic N are advantageous for the Co_3O_4 growth. Furthermore, the N modification is effective in reducing the oxygen content of chemically prepared graphene and hence is good for Co_3O_4 dispersion and the amelioration of first cycle efficiency, demonstrating the potential of NMEG based composite as high performance Li-ion battery anode materials.

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Introduction

The increasing demand in the fields of electronic vehicles, portable electronics, and stationary power grid energy storage requires reliable energy storage devices. Rechargeable lithium ion batteries (LIB) are one of the most promising ones. Graphite is commonly used as a reliable anode material in commercial LIBs with good cyclability and safety. However, graphite has a limited theoretical capacity of 372 mAh g^{-1} and it is necessary to further improve its performance to meet the requirement of dramatically increased demands [1]. Considerable research efforts have been made in developing new electrode materials with high energy and power densities, [2] including graphene/transition metal oxide combinations, [3] surface-modified graphite, [4] and multi-functional hybrid nanostructured materials [5-7].

Graphene is an allotrope of carbon, with atoms bonded in hexagonal sp^2 arrangement to form a 2-dimensional (2D) carbon sheets. The unique properties of graphene, such as high surface area, [8,9] excellent conductivity, [10,11] and wide electrochemical potential window, [12] have attracted intense research interest on its synthesis, characterization, and exploration of energy storage applications [11-13]. Preparation of various graphene/transition metal oxide (SnO_2, [14] TiO_2, [15] Fe_2O_3, [16] Co_3O_4, [17] Mn_3O_4, [18] NiO [19]) composites, and their applications as anode material for LIBs are vastly reported in recent years. Among these graphene/transition metal oxide composites, Co_3O_4/graphene shows excellent performance [17,20-24]. However, it is worth to note that, the above mentioned composites, including pure chemically derived graphene [25-27] suffer from high initial capacity loss due to large surface area of graphene, possible defects and surface electrolyte interface (SEI) formation. For LIBs cells composed of Li-containing transition metal oxides ($LiFePO_4$, $LiMnO_2$, or $LiCoO_2$) as cathode [2] and garphene/transition metal oxide composites as anode, [7] Li-ions as the charge carrier transfer between the cathode and anode, resulting in red-ox reactions or intercalation processes at the electrodes. In the first charge/discharge cycle, some Li ions react with organic electrolyte and anode material, forming SEI layer on the anode surface and causing irreversible capacity loss [28]. As in these LIBs cells the Li-containing transition metal oxide cathode which has limited Li atoms is the only source of Li ions, the irreversible reaction of Li ions with anode, or the exhaustion of Li during cycling will directly decrease cell capacity and energy density [29]. The first cycle efficiency, i.e. the ratio of discharge over charge current, together with the cycle stability as well as the rate capacity, are critical evaluation parameters of the electrode materials for practical application. Chemically derived graphene has abundant dangling bonds, defects, oxygen-containing functional groups, all of which have higher reactivity toward the electrolytes and Li ions, and can easily result in the large irreversible capacity loss in the initial cycle. Furthermore the oxygen released from decomposition of O-containing functional groups may partly oxidize the electrolyte, and cause cell instability and capacity degradation [30].

Wang et al. reported that the capacity of graphene was 945 mAh g^{-1} in the first cycle, which was close to the theoretical capacity of 748 mAh g^{-1} probably because Li ion could be incorporated on both sides of graphene, and maintained 460 mAh g^{-1} after 100 cycles [31]. The first discharge and charge capacities of few-layer graphene sheets were 2035 and 1264 mAh g^{-1} respectively [26]. By introducing heteroatom doping [5,32] or combination with various metal/metal oxides [33] the capacity of graphene could be greatly enhanced. Graphene doped with N was reported to deliver a reversible capacity of 872 mAh g^{-1}, however the discharge capacity in the first cycle was around 2127 mAh g^{-1} with 1255 mAh g^{-1} of initial irreversible capacity loss [30].

Here we report an electrode prepared from microwave exfoliated graphite oxide (MEGO). In order to reduce the effect of O-containing groups, N doping was conducted to introduce N atoms to MEGO (abbreviated as NMEG in this manuscript). The Co_3O_4 nanoparticles were grown on NMEG with different weight ratio, and the effect of the Co_3O_4 weight ratio on the first cycle efficiency and rate performance of Co_3O_4/NEMG composite was investigated. The first cycle efficiency of Co_3O_4/NMEG composite with Co_3O_4 weight ratio of 10%, 40%, 70% and 100% was 50.4 ± 2.4, 73.7 ± 1.6, 77.3 ± 1.3%, and 64.0 ± 1.5 respectively. After 100 cycles, the capacity of Co_3O_4/NMEG composite with Co_3O_4 weight ratio of 10%, 40%, 70% and 100% was 823, 762, 910 and 295 mAh g^{-1} respectively, at a current density of 63 mA g^{-1}. 70% Co_3O_4/NMEG was the best sample in this series, delivering the largest reversible capacity of 910 mAh g^{-1} and highest first cycle efficiency of 77.3 ± 1.3%, with an electrode active material loading of 1.2-1.8 mg for 2032 type coin cell. For comparison, the first cycle efficiency of 70% Co_3O_4/tR-G-O (thermal reduced graphene) electrode was 51.3 ± 2.5 only. These results indicate that the N modification is effective to ameliorate the poor first cycle efficiency of those chemically derived graphene composite. N-doped graphene composite has a high potential to use as high performance LIBs anode materials for practical application.

Experimental section

Microwave exfoliated GO was synthesized as described previously [34,35]. Briefly, GO powders synthesized from modified Hummers' method were irradiated in a domestic microwave oven operated at 1100 W for 1 min, [34] and expanded in microwave rapid heating to form a fluffy microwave emission GO (MEGO) powder. The MEGO powder was further annealed at 850 °C for 1 h in a mixed gas of NH_3 and Ar (1:2 v/v) with a total gas flow rate of 180 mL min^{-1}, and dried after washing by large amount of DI water. In a typical preparation process of Co_3O_4/NMEG, 200 mg of NMEG was dissolved in 50 mL of DI water, followed by addition of 75, 450, 1400 mg of $CoCl_2$ $6H_2O$ and 100, 850, 1800 mg of urea to obtain Co_3O_4/NMEG with Co_3O_4 weight ratio of 10%, 40% and 70% respectively. The resulted solution was refluxed under 90 °C with magnetic stirring for 3 h to form $Co(OH)_2$/NMEG. $Co(OH)_2$/NMEG was collected by filtration, and dried in an oven at 60 °C overnight. Finally the Co_3O_4/NMEG was produced by annealing $Co(OH)_2$/NMEG at 300 °C in N_2 for 4 h.

Co_3O_4/tRG-O sample was synthesized in a similar procedure, except that NMEG was replaced by thermally reduced G-O (tRG-O), which was made by annealing GO at 850 °C