Superior electrochemical properties of manganese dioxide/reduced graphene oxide nanocomposites as anode materials for high-performance lithium ion batteries

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HIGHLIGHTS

- MnO_2/rGO nanocomposites were synthesized via a simple solution method using CTAB.
- MnO_2/rGO nanocomposites have a large specific surface area and mesoporous structure.
- GITT revealed that MnO_2/rGO nanocomposites have superior kinetic properties.
- Unique structural properties provide superior rate capability and cyclability.

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ABSTRACT

MnO_2/reduced graphene oxide (rGO) nanocomposites were synthesized via a simple solution method at room temperature for use in Li-ion batteries. Owing to the mesoporous features as well as the high electrical conductivity of rGO, the overall electronic and ionic conductivities of the nanocomposite were increased, resulting in improved electrochemical properties in terms of specific capacity, rate capability, and cyclability. In particular, as-prepared nanocomposites showed 222 and 115 mAh g^{-1} at a current density of as high as 5 and 10 A g^{-1}, and the specific capacitance was well maintained after 400 cycles. In addition, MnO_2, via composite formation with rGO, permitted the additional conversion reaction between MnO and Mn_3O_4, resulting in the reduction of the initial irreversible capacity despite the high first discharge capacity caused by the large specific surface area.

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1. Introduction

Lithium-ion batteries (LIBs) with high energy density have attracted considerable research attention owing to the increasing demand for compact and long-life electronic devices [1,2]. To obtain high-performance LIBs, electrode materials with high specific capacity and satisfactory cycle life are essential [3]. Among various potential electrode materials, transition metal oxides such as TiO_2 [4—7], Fe_3O_4 [8—10], SnO_2 [11—13], and Co_3O_4 [14—17] have been studied widely owing to their high theoretical capacity (>700 mAh g^{-1}) based on the conversion reaction and natural abundance of anode materials in a LIB. In particular, manganese dioxide (MnO_2) has attracted much attention owing to its high theoretical capacity (1230 mAh g^{-1}), low cost, and eco-friendliness. However, simplex MnO_2 electrodes suffer from low electrical conductivity and volume expansion and aggregation during cycling, resulting in poor rate capability and rapid capacity fading. In addition, their low initial efficiency limits practical applications [18—20]. To overcome these problems, carbonaceous materials with high electrical conductivity and adequate ductility have been

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widely employed as matrices in metal oxides to improve their cycle performance [21–33].

Graphene, with a two-dimensional honeycomb sp^2 carbon lattice, has attracted considerable attention owing to its properties and potential applications in many fields such as lithium batteries [34], sensors [35], supercapacitors [36], and hydrogen storage [37]. Among various carbon nanostructures, graphene is expected to be an excellent template for nanocomposites as LIB anodes owing to its superior electrical conductivity, large surface area, structural flexibility, and chemical stability [38–40].

In this light, a few studies have already focused on MnO_2/graphene composites for anode materials. For example, Li et al. reported an MnO_2/3D porous graphene-like composite (3D PG-Mn) with initial capacity of 914 mAh g^{-1} at a rate of 100 mAh g^{-1}; the capacity sharply decayed to 433 mAh g^{-1} at a rate of 1600 mA g^{-1}, and capacity retention of 84.6% was reported after 200 cycles at 100 mA g^{-1} [30]. Sui et al. reported an MnO_2/nitrogen-doped graphene composite with reversible specific capacity of 1003 and 636 mAh g^{-1} at a rate of 100 and 1500 mAh g^{-1}, respectively [31]. Li et al. fabricated a graphene-wrapped MnO_2-graphene nanoribbon composite in which graphene flakes tightly sandwiched nanosized MnO_2 that grew directly on the graphene nanoribbons; this nanocomposite showed specific capacity of 672 mAh g^{-1}, and the capacity decreased to 300 mAh g^{-1} at a rate of 1000 mA g^{-1} [32]. Yu et al. synthesized a free-standing layer-by-layer graphene-MnO_2 thin film that showed specific capacity of 686 mAh g^{-1} at a rate of 100 mA g^{-1} and capacity retention of 72% after 40 cycles with varying current rates from 100 to 1600 mA g^{-1} [41]. Although these materials showed better electrochemical properties compared to bare MnO_2 particles, they have limited rate capability and cyclability despite the low loading amount of MnO_2 in the composites (i.e., <70 wt%) [30–32,41].

In this study, we report the fabrication of MnO_2/rGO composites via a simple solution method using cetyltrimethylammonium bromide (CTAB). Uniform adsorption of CTAB on the rGO surface led to the homogeneous deposition of MnO_2, and CTAB could prevent the direct redox reaction between carbon and MnO_4^- [42]. In the composite, rGO can provide a highly conductive structure with large surface area to support well-contacted MnO_2 nanoparticles. In addition, it effectively enhances the mechanical strength of the nanocomposite during volume changes and suppresses the aggregation of MnO_2 nanoparticles during Li ion insertion/extraction. This results in superior rate capability and cyclability despite the high MnO_2 loading amount in the composite (i.e., 75 wt%). In addition, the smooth penetration of Li^+ ions through mesopores and high electrical conductivity of the rGO template improved the kinetic properties and led to the additional conversion reaction between MnO and Mn_3O_4 in the nanocomposite, resulting in the reduction of the initial irreversible capacity. In particular, we revealed the origin of the additional conversion reaction between MnO and Mn_3O_4 in the MnO_2/rGO nanocomposite by using the galvanostatic intermittent titration technique (GITT).

2. Experimental section

2.1. Preparation of rGO nanosheets

Graphite oxide (GO) was synthesized from purified natural graphite powder (≤45 μm, Aldrich) by a modified Hummers method as described previously [39]. rGO nanosheets were produced by a solid-state microwave irradiation method as reported previously [43]. Briefly, 90 wt% of GO powder was uniformly mixed with 10 wt% rGO powder using a ball-miller. The resulting GO/rGO mixture was placed in a quartz bottle and covered with a lid inside a glove box. The quartz bottle was filled with Ar gas in the glove box

to prevent the oxidation of carbon and then sealed tightly. The GO/rGO mixture in the quartz bottle was then placed in a microwave oven (Mars 5, CEM) and subjected to pulsed irradiation at 1600 W.

2.2. Synthesis of MnO_2/rGO nanocomposite and bare MnO_2 nanoparticles

$$4KMnO_4 + 3C_2H_5OH \rightarrow 4MnO_2 + 3CH_3COOH + 4KOH + H_2O \quad (1)$$
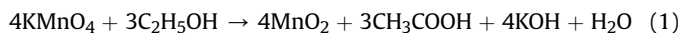
For preparing the MnO_2/rGO nanocomposite, CTAB (Aldrich) was used as a surfactant and protection layer to prevent direct contact between rGO and MnO_4^- ions. First, 43.5 mg of rGO was dipped into 1 wt% CTAB aqueous solution, and the solution was ultrasonicated to obtain a uniformly dispersed rGO/CTAB suspension. Next, 15 mL of 0.1 M $KMnO_4$ solution was added to the rGO/CTAB suspension and stirred for 1 h. Then, ethanol was slowly added to the solution to reduce MnO_4^- ions to MnO_2 until the purple color disappeared. The MnO_2 formation mechanism is shown above in equation (1). After washing with ethanol, ammonium nitrate was added to remove residual CTA^+ ions by ion exchange reaction between CTA^+ ions and NH_4^+ ions [44]. The final product was washed repeatedly with distilled water and ethanol and then dried at 80 °C for 24 h. The detailed synthetic mechanism is reported in our previous research that reports the synthesis of MnO_2/CNT nanocomposites [45]. For comparison, bare MnO_2 nanoparticles were similarly synthesized; 60 mL of ethanol was added to 150 mL of 0.01 M of $KMnO_4$ aqueous solution and maintained at 25 °C for 8 h under stirring. During the synthesis, the temperature of the solution was maintained at 25 °C using a circulator.

2.3. Material characterization

X-ray diffraction (XRD, Rigaku, CuKα, 40 kV, 20 mA) patterns were obtained in the 2θ range between 10° and 80° at intervals of 4°/min at room temperature. Raman spectroscopy (T64000, Jobin-Yvon) was also used to confirm the phase of MnO_2. N_2 adsorption−desorption isotherms were measured using a Micromeritics ASAP ZOZO instrument at 77 K, and the surface areas were calculated by the Brunauer−Emmett−Teller (BET) method.

The morphology of the as-prepared samples was characterized by transmission electron microscopy (TEM, JEM-ARM 200F). To determine the MnO_2 content in the composite, TGA data were obtained using a thermal analysis instrument (TGA/DSC 1, Mettler Toledo) with a heating rate of 10 °C min^{-1} under an air flow rate of 50 mL min^{-1}. Elemental analysis (EA) measurements were performed to quantify the carbon contents in the MnO_2/rGO nanocomposites.

2.4. Electrochemical test

The electrochemical properties were investigated using CR2032 coin-type cells that were assembled in an argon-filled glove box with lithium foils as the counter electrode and 1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (EC:DMC, 1:1 in volume) as the electrolyte. The working electrode of the MnO_2/rGO nanocomposite was prepared by mixing 90 wt% of the active composite and 10 wt% of polyvinylidene difluoride (PVDF, Alfa Aesar) dissolved in N-methyl-2-pyrrolidone (NMP, Sigma−Aldrich) to form a slurry that was then coated on a copper foil substrate. For comparison, the electrode of bare MnO_2 nanoparticles was fabricated with 10 wt% of binder and 22.5 wt% of carbon black. The carbon amount in both the MnO_2/rGO composite and the electrode made of bare MnO_2 nanoparticles was the same. The mass loading and