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Nanoscale MnO and natural graphite hybrid materials as high-performance anode for lithium ion batteries

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ABSTRACT

In this work, MnO and natural graphite (NG) hybrid composite was synthesized via a hydrothermal reaction and a subsequent self-reduction process. As an anode material for lithium ion batteries, MnO/NG composite displays excellent cycling stability and good rate capability. The charge–discharge test showed the highest initial lithiation/delithiation specific capacities of 552.8 and 511.7 $\text{mAh} \cdot \text{g}^{-1}$, which were maintained at 494.9 and 497 $\text{mAh} \cdot \text{g}^{-1}$ even after 120 cycles, at 0.2 *C* with a voltage range from 0.01 V to 2.0 V. The lithiation specific capacity was retained 280 $\text{mAh} \cdot \text{g}^{-1}$ at 10 *C*, which extremely precedes the bare NG materials.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been attracting considerable attention in the mark of energy storage for portable electronic devices and electric vehicles because of their high energy density, high operating voltage, and low self-discharge rate [1–3]. Although the performance of LIBs continues to improve, developing novel structures of electrode materials is still the largest challenge [4–9]. To date, many anode materials, such as carbon-based materials [10–11], silicon-based materials [12–14], metal oxides [15–17], alloys [18–20], and their composites, have been exploited [21–25]. However, only several materials among them achieved commercial utilization [26]. Nature graphite (NG) is still the potential anode material for commercial LIBs because of its high electrical conductivity, high coulombic efficiency, lower reaction potential, and low cost [27]. Its electrochemical properties have been widely and systematically investigated for commercial utilization. However, the theoretical specific capacity of NG is only 372 mAhg^{-1}, and the commercial use of NG is currently limited by its poor rate capability and cycle performance in practical conditions [28]. To improve the performance of NG electrodes, many efforts are underway to expose the defects, and nanomaterials on the surface or in the intercalation of NG have been investigated [29–32].

Transition metal oxides are promising anode materials for high performance LIBs because of their high theoretical capacity [33]. Among the various transition metal oxides, MnO has attracted considerable interest owing to its high theoretical capacity, low operation potential, natural abundance, and environmental benignity [34–36]. Nevertheless, as an anode material for LIBs, bare MnO still suffers from fast capacity fading and low rate capability, which are caused by poor electronics, serious agglomeration, and large volume change during the charge/discharge process [37]. According to the primary advantages of NG and MnO, the strategy of depositing MnO on the surface or in the intercalation of NG, which forms the NG-based composite, may be an effective route to obtain enhanced lithium storage properties. Moreover, in comparison to that of their pristine counterparts, the electrochemical performance of the composite is obviously improved.

Herein, we report a facile hydrothermal reaction route combined with a subsequent self-reduction process for fabricating the NG-based MnO/NG composite. The MnO/NG composites, as anode materials for LIBs, exhibit high capacity and impressive rate capability, which may be the synergetic effects of MnO and NG.

2. Experimental Section

2.1. Materials preparations

Spherical NG (1.0 g) (D_{50} = 17 μm, carbon content > 99.95%) and different stoichiometric ratios of $KMnO_4$ powders (0.1 g, signed

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NG-1; 0.15 g, signed NG-2; 0.2 g, signed NG-3) were first mixed in 200 mL deionized water and then ultrasonically treated for 0.5 h to form a black-red dispersion. Subsequently, the mixture was poured into a sealed Teflon-lined stainless steel autoclave and kept at 160 °C for 10 h. After cooling to room temperature, the black precipitate was collected by filtration, washed several times with deionized water, and dried in an oven at 80 °C for 4 h. Finally, all products were self-reduced and calcinated at 700 °C for 3 h under argon atmosphere to obtain the MnO/NG composites.

2.2. Materials characterizations

The materials were characterized by X-ray diffraction measurement (XRD, Bruker D8 Advance using Cu Ka radiation, within the 10.00°-80.00° 2θ range), scanning electron microscopy (SEM, JSM-6700F), inductively coupled plasma emission spectroscopy (ICP, OPTIMA 8000DV.) and Raman measurements (Raman, LabRAM HR Evolution, equipped with a laser that provide excitation wavelengths at 633 nm). X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu group company) using a monochromatic Al Ka radiation ($h\gamma = 1486.6$ eV). The binding energies of the samples were calibrated by taking C1s peak as a reference (284.6 eV).

2.3. Electrochemical measurements

The electrochemical performance of the MnO/NG composites were carried out using standard R2016 type coin cells. The working electrodes were prepared by mixing 85 wt% MnO/NG composites with 5 wt% conductive carbon Super-P and 10 wt% polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP) solvent. The viscous slurry was coated onto a copper foil substrate and dried in a vacuum oven at 80 °C for 10 h. The obtained film was cut into discs, the mass was about 2.0 mg and the diameter was 1 cm. A Celgard 2400 member was used as separator. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbinate (DEC) (1:1:1 by volume). Lithium foil was used as the counter and reference electrode. The cells were assembled in an argon-filled glovebox. The discharge and charge experiments were carried out between 0.01 and 2.0 V (vs. Li^+/Li) using a Land CT2001A equipment. All the capacity values were calculated based on the mass of the MnO/NG composites. The cyclic voltammetry (CV) measurement was performed on CHI660E electrochemical workstation with the voltage range from 2.0 to 0.01 V at a scanning rate of $0.1\ mV \cdot s^{-1}$. The electrochemical impedance spectroscopy (EIS) was carried out also on CHI660E electrochemical workstation at an amplitude of 5 mV and frequencies range of 100 KHz –100 mHz.

3. Results and discussion

Typically, in the fabrication process of the MnO/NG composite, NG is initially oxidized partially by the strong oxidant $KMnO_4$, and then MnO_4^- is reduced to form MnO_2, which is deposited onto the surface of NG [38–39]. Subsequently, the resulting MnO_2/NG composite is sintered at 700 °C for 3 h under argon atmosphere, leading to the formation of the MnO/NG composite. Here, NG was not only the composite substrate but also the reducing agent.

XRD patterns of the as-synthesized MnO/NG composites are shown in Fig. 1a, where two well-defined peaks were noted at 26.5° and 54.8°, corresponding to the (002) and (004) planes of the NG (JCPDS, No. 65-0380). However, no obvious peaks correspond to MnO because of its low content. The contents of MnO in the MnO/NG products are evaluated to be about 2.1, 4.2, and 6.3 wt.% for NG-1, NG-2 and NG-3 by ICP analysis, respectively. However, when we enlarged the 2θ range from 34° to 42° (Fig. 1a, inset), the diffraction peaks emerged at 35.0° and 40.6° were assigned to the (111) and (200) planes of MnO (JCPDS, No. 44-0141), respectively.

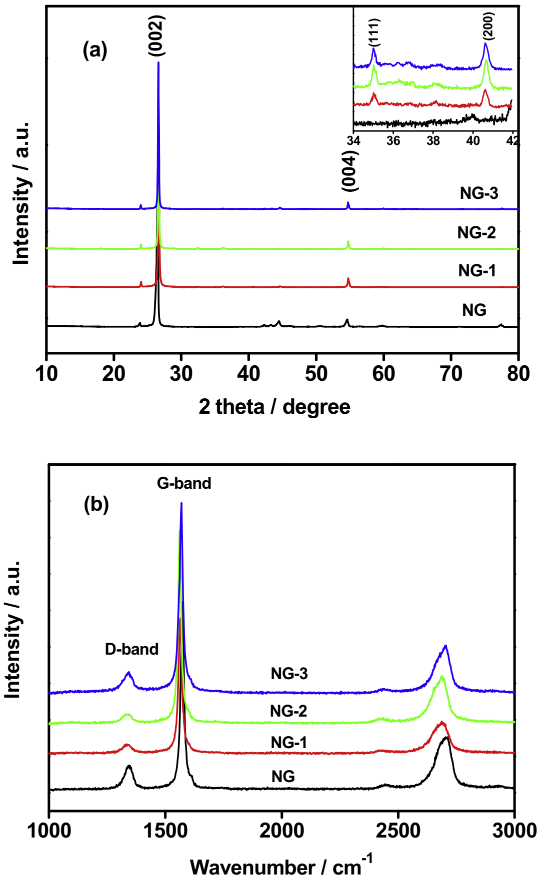

Fig. 1. XRD patterns (a) and Raman spectra (b) of NG and MnO/NG composites

Raman spectra were performed to investigate the structural changes during the synthesis processing from NG to MnO/NG composite (Fig. 1b). The G and D bands of NG were ascribed to ordered sp2 bonded carbon and defects carbon [28], respectively. The existing G band at 1573 cm^{-1} and D band at 1343 cm^{-1} in the spectrum of NG indicate that the ordered sp2 bonded carbon dominates the structure of the planes. After the formation of the MnO/NG composite, the G band weakened, whereas the D band became increasingly strong. The D/G intensity of the MnO/NG composites ($I_D/I_G = 0.24$, for NG-1; $I_D/I_G = 0.26$, for NG-2; $I_D/I_G = 0.37$, for NG-3) were larger than that of NG ($I_D/I_G = 0.14$), which indicated that the processes of forming composites increase the disorder degree of the planes and the exfoliation of NG [40]. Furthermore, the high value of I_D/I_G suggests the existence of nongraphitic carbon in the MnO/NG composites, which possess significantly higher lithium storage performance than graphitic carbon [41].

To further investigate the oxidation and the composition of the NG-3, XPS analyses were carried out. As shown in Fig. 2, the XPS spectrum confirmed the presence of Mn, C, and O elements. The high-resolution Mn2p spectrum (Fig. 2b) displays two peaks at 641.6 eV for $Mn2p_{3/2}$ and 653.4 eV for $Mn2p_{1/2}$, respectively, which are characteristic of MnO [42]. The C1s spectrum is shown in Fig. 2c, and the high-resolution C1s spectrum can be deconvoluted into three peaks. The strong peak at 284.6 eV may be attributed to the graphitic carbon in NG, whereas the weaker ones may be attributed to the oxygenated carbon atoms (285.5 eV for C–O; 288.8 eV for O–C=O), which indicate the existence of some residual oxygen