

Synthesis and electrochemical performance of MoO₂/graphene nanomaterials as anode for lithium-ion battery

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Abstract

In this articles, molybdenum dioxide/graphene composites were successfully prepared by a hydrothermal method. The results indicated graphene composition affects the properties of the electrochemical electrode, increased to 10 wt%, the molybdenum dioxide particles were uniformly deposited on the graphene sheets. The samples used as the electrode material for lithium batteries; it exhibited high reversible specific capacities of 1267 mAhg⁻¹ at the second cycle and 629 mAhg⁻¹ after 60 cycles. The outstanding electrochemical performance of the composite can be attributed to the synergistic interaction between molybdenum dioxide and graphene. There were enough void spaces to buffer volume change in the structure. Furthermore, graphene nanosheets in the hybrid material could act as not only lithium storage electrodes but also electronic conductive channels to improve the electrochemical performances.

Keywords. Molybdenum dioxide, graphene composites, lithium-ion batteries.

1. INTRODUCTION

Rechargeable lithium ion batteries (LIBs) have become one of the most promising types of battery technology for electrochemical energy storage due to their high energy density, low maintenance, and relatively low self-discharge [1, 2]. However, in the classical commercial LIBs, graphitic carbon was the most popular electrode material, which only delivers a theoretical specific capacity of 372 mAhg⁻¹ [3].

Developing new electrode materials with high energy densities has been an important way to satisfy the ever-growing demand for high-performance LIBs. Nowadays, nanostructured transition-metal oxides have been regarded as high capacity anodes, due to the higher capacity than that of graphite [4-6]. Among them, molybdenum dioxide (MoO₂) has attracted much attention, owing to its appealing features, including low resistance, short diffusion path and large surface area [7].

Although most pure MoO₂ nanostructures have the high specific capacity and mitigated pulverization, the cycling stability is still not satisfied [8]. Nano-structured MoO₂ hybridized with conductive and elastic carbon was an effective strategy to improve the structural integrity as well as the cycling performance [9]. Recently, a number of metal oxide/graphene hybrids have been reported,

including Fe₃O₄, Mn₃O₄, and Co₃O₄ which can obtain better electrochemical properties than that of counterpart [6, 10, 11].

In this work, MoO₂/graphene nanocomposites were prepared by the hydrothermal process from a precursor solution which was obtained by adding reducing agent and graphene turbid liquid into peroxy-polymolybdic acid. The effects of hydrothermal time and the mass ratios of MoO₂ to graphene on the growth of MoO₂ crystal and electrochemical properties have been studied.

2. EXPERIMENTAL

2.1. Preparation of MoO₂ particles

MoO₂ nanoparticles were prepared via hydrothermal method. 10 mL 30 % H₂O₂ was added onto 1 g Mo with continuously stirring until the clear orange sol was obtained. Then the sol was mixed with 20 mL ethanediol and 50 mL deionized water. Stirring the sol for about 30 min until the sol turned into clear and yellow mixture, which was directly transferred into a Teflon-lined autoclave and reacted at 180 °C for 72 h. Finally, the samples were centrifuged and washed with ethanol and distilled water for three times. After drying at 60 °C in vacuum condition for 24 h, the black powder was obtained.

2.2. Preparation of MoO₂/Graphene Composites

Graphene oxide (diameter of 50-100 nm, thickness of 0.8 nm, 80 % single layer ratio, 99 % purity, BET surface area of 500-600 m² g⁻¹) was purchased from Nanjing XF NANO Co. Ltd.

The composites were prepared by hydrothermal again. Firstly, 0.2 g as-prepared MoO₂ was dispersing in 30 mL ethanediol. Then various volumes of GO suspension were added sequentially under vigorously stirring. Then the L-ascorbic acid was added into the mixture. Afterwards, HCl aqueous solution was dropwise added with magnetic stirring until the pH value became 1. The mixture was transferred into a Teflon-lined autoclave after sonicated for 30 min and reacted at 180 °C for 10 h. Finally, the samples were centrifuged and washed with ethanol and distilled water for three times. After drying at 60 °C in vacuum condition for 24 h, the black powders were obtained.

2.3. Characterization

X-ray powder diffraction patterns of the prepared samples were recorded using a diffractometer (XRD; model X'pert PRO-PANalytical, Netherlands). The structure of samples was observed using field emission scanning electron microscopy (FESEM; model No. JSM-6700F, Japan). Raman spectroscopy equipped with a 633 nm laser (Raman; model Renishaw Invia, Britain) was employed to get the structural information.

2.4. Electrochemical measurements

The electrochemical tests were performed via CR2025 coin-type test. To fabricate the working electrodes, 70 wt% active material (MoO₂ or MoO₂/graphene), 25 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) were mixed, then compressed it into a lamella about 0.2 mm in thickness and cut it into a wafer about 1 cm² in area. Pure lithium foil was used as both counter and reference electrode. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC)+dimethyl carbonate (DMC)+ ethylmethyl carbonate (EMC) (1:1:1 in volume). A Celgard 2300 membrane was used as the separator. The galvanostatic discharge/charge cycles were carried out on a XINWEI system over a voltage range of 0 to 3.00 V at room temperature. Cyclic voltammetry (CV) tests were performed on an Autolab Potentiostat 30 system. The specific capacities in this article were calculated based on the overall mass of the composite.

3. RESULTS AND DISCUSSION

3.1. FESEM

Figure 1 shows the FESEM images of the MoO₂/graphene with different amount of graphene. As seen from Figure 1(a), a curled morphology of graphene sheets consisting of the thin wrinkled structures is observed. When the amount of graphene increases to 10 wt%, the molybdenum dioxide particles are uniformly deposited on the graphene sheets. However, both the graphene and MoO₂ particle have obvious agglomeration when the weight ratio of graphene sequentially increasing to 15 wt%.

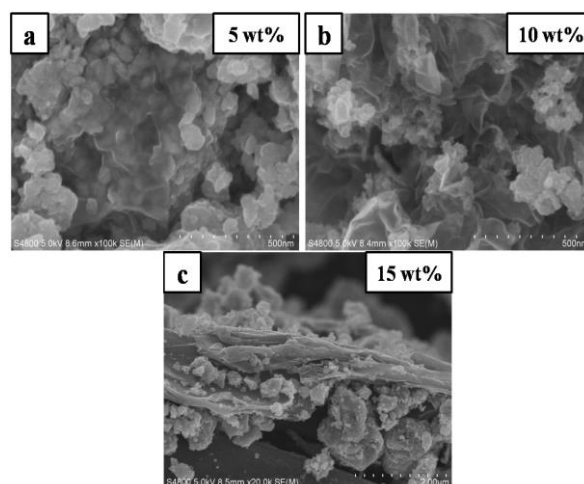


Figure 1: FESEM images of MoO₂/graphene with different weight ratios

3.2. X-ray diffraction (XRD)

Figure 2 shows the X-ray diffraction (XRD) patterns for the as-prepared MoO₂/graphene. All the diffraction peaks are readily indexed to a pure monoclinic MoO₂ (JCPDS No. 78-1073, $a = 5.660$ Å, $b = 4.860$ Å, $\beta = 120.94^\circ$).

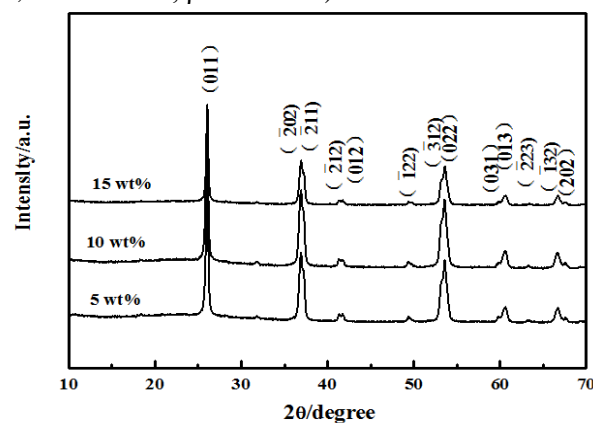


Figure 2: XRD patterns of MoO₂/graphene composites with different weight ratios

The diffraction peaks from the graphene sheets are not clearly observed in the pattern due to their weak crystalline and the overlap of the weak diffraction of the graphene sheets at 2θ of 26.6 degree with that of MoO_2 [13, 14]. The XRD patterns also show that the crystal structure of monoclinic MoO_2 is not changing with the increase of the graphene.

3.3. Raman spectroscopy

The structure of the composite was further characterized by Raman spectroscopy. As shown in Figure 3, the peaks appear at 992, 818, 662, 335 and 282 cm^{-1} refer to M=O stretch (A_g, ν_s), M=O stretch (A_g, ν_{as}), O-M-O stretch (B_{2g}, B_{3g}, ν_s), O-M-O bend (A_g, B_{1g}, δ), and O=M=O wagging (B_{2g}, δ) [12, 13], respectively.

The peaks at 1586 and 1344 cm^{-1} correspond to G band (E_{2g} symmetry, in-plane bond-stretching motion of pairs of sp^2 C atoms) and D band (defect-related) of graphene sheets [14, 15]. The characteristic peaks of MoO_2 particles and graphene appear at the same time, suggesting the formation of the MoO_2 /graphene composite [16].

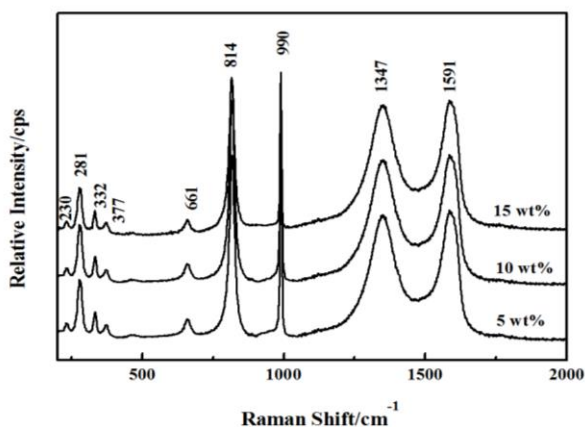


Figure 3: Raman spectra of MoO_2 /graphene with different weight ratios

3.4. Electrochemical performances and reaction mechanism

The cycle performance of the composites with 5, 10 and 15 wt% is shown in figure 4. The different capacities indicate the influence of graphene content in the composites on battery electrochemical performance. The capacity of the composite with less graphene (5 wt% graphene) shows capacities of 864 mAhg^{-1} at second cyclic and 461 mAhg^{-1} after 60 cycles. When increasing the amount of graphene to 10wt%, there is much higher capacity of 1267 mAhg^{-1} at the second cycle and 629 mAhg^{-1} after 60 cycles. The capacity of the composite with

15 wt% graphene is 621 mAhg^{-1} at second cycle, but it decays to 95 mAhg^{-1} after 60 cycles. In the other words, the capacity depends on the weight ratios of MoO_2 and graphene in the composites, and the capacity is highest when the amount of graphene is 10 wt%.

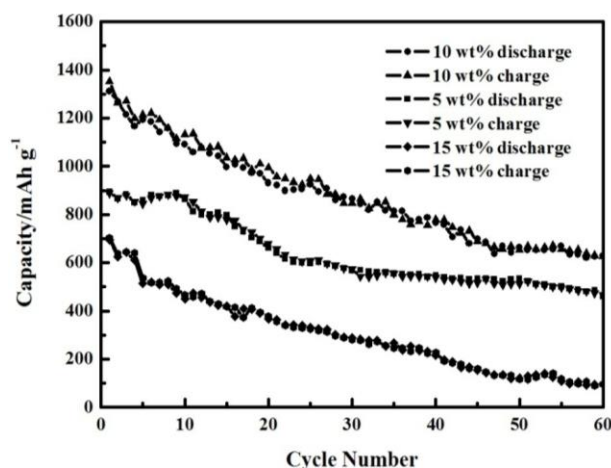
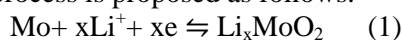


Figure 4: Cycling performance of MoO_2 /graphene composites with 5 wt%, 10wt%, and 15 wt%, at $0.1 \text{ mA}\cdot\text{cm}^{-2}$

Figure 5(a) shows the CV curves for the electrode made of the MoO_2 /graphene composite (10 wt% GO in the composite) at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$. In the first discharge cycle, there is a broad reduction peak at $\sim 0.85 \text{ V}$ reflecting the irreversible reduction of electrolyte [17]. The CV curves remain almost the same from the second cycle onwards, indicating a highly reversible reduction and oxidation process of the as-prepared MoO_2 /graphene composite [18]. The charge and discharge profiles for of the composite with 10 wt% GO for the 1st, 2nd, 20th, 40th, and 60th cycles at a voltage range of 0 V and 3.0 V versus Li^+/Li , and a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ are shown in Figure 5(b). In the first cycle, a short discharge plateaus at 0.85 V is observed and it is in agreement with the CV curves.

As shown in Figure 5(b), the discharge capacities of the electrode in the 1st, 2nd, 20th, 40th and 60th cycles are 1311, 1265, 931, 766 and 629 mAhg^{-1} , respectively, and the charge capacities of the electrode in the 2nd, 20th, 40th, and 60th cycles are 1271, 954, 778 and 626 mAhg^{-1} , respectively. From the first cycle onward, 49.7% discharge capacity and 49.25% charge capacity are retained up to the 60th cycle with a Columbic efficiency of nearly 100%. According to previous research [19], the reaction between MoO_2 and Li^+ during the charge and discharge process is proposed as follows:



In this paper, the x can be up to 3 at 60th cycle.

Theoretically, the capacity of MoO₂ is 838mAhg⁻¹, and which of the carbon material is 372mAhg⁻¹. The theoretical capacity of composite could be calculated as MoO₂ wt% × 838 mAhg⁻¹ + carbon wt% × 372 mAhg⁻¹ [20], and the theoretical capacity of composites with 10 wt% graphene is 791.4 mAhg⁻¹. However, in the first cycle the discharge capacity is higher than the theoretical value. The extra capacity may arise from reversible reaction of lithium with the active surface groups of graphene (C-H and C-OOH bonds) [13, 19]. After 35 cycles, the actual capacity approaches to the theoretical value.

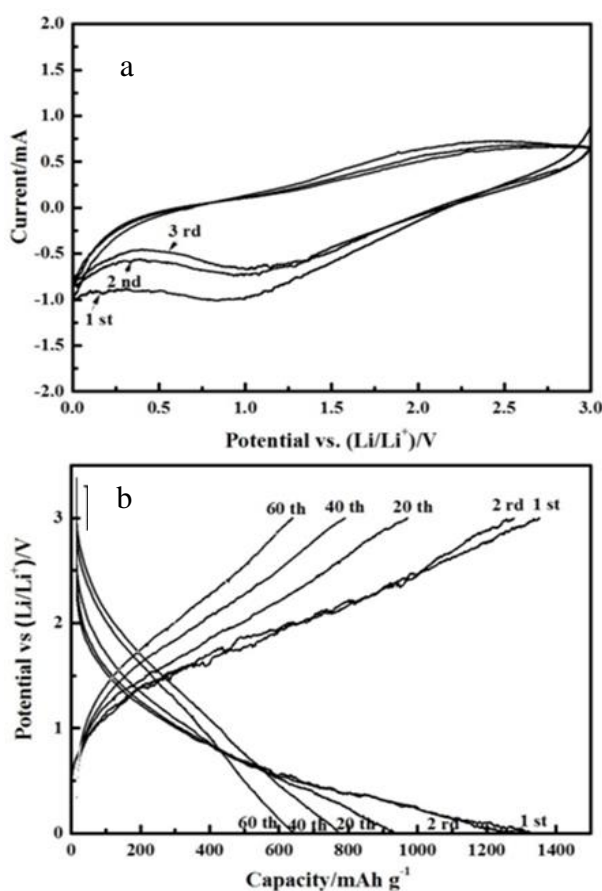


Figure 5: Electrochemical performance of the MoO₂/GO composites with 10 wt% graphene (a) cyclic voltammograms at a current density of 0.1 mA·cm⁻² (b) The relation of the galvanostatic voltage versus the capacity

The outstanding electrochemical performance of the composite can be attributed to two reasons. Firstly, a dimensional confinement of the MoO₂ particles by the surrounding graphene prevented the volume expansion upon lithium insertion. As pointed out before, the main reason for rapid fading of MoO₂ electrode was that a large volume expansion of the MoO₂ material occurs during the

cycling [16, 18, 21]. In the above FESEM images, graphene nanosheets are homogeneously distributed between MoO₂ particles in the structure of the composite with 10 wt% graphene, so the stress formed during the process of lithium insertion was avoided. Even though the volume expansion has happened, the electrode was not pulverized because there were enough void spaces in MoO₂/graphene to buffer volume change. Secondly, the graphene also has made MoO₂ electrochemically active since charge carriers could be effectively and rapidly conducted back and forth from the MoO₂ nanoparticles to the current collector through the highly conducting the graphene network.

4. CONCLUSION

The molybdenum dioxide/graphene composites were synthesized by hydrothermal method, which is the nanostructures formed by MoO₂ nanoparticles deposited on the graphene sheets. The discharge/charge property of the MoO₂/graphene nanocomposite was studied by galvanostatic charge-discharge measurement as an anode material for lithium batteries, CR2025 cell, exhibited high reversible specific capacities of 1267 mAhg⁻¹ at the second cycle and 629 mAhg⁻¹ after 60 cycles. The improved capacity of MoO₂/graphene may be attributed to the synergistic interaction between molybdenum dioxide and graphene.

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