Two-phase Solvothermal Synthesis of MoO$_2$/RGO Nanocomposites for Lithium-Ion Battery Anodes

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Abstract. Nowadays, it is necessary to develop the lithium-ion battery with higher capacity, lighter weight and thinner volume. Transition metal oxide, as a promising anode materials, has drawn much attention, as a result of its large capacity and high economic value. However, poor cycle stability greatly limits its practical applications. In this paper, MoO$_2$/RGO nanocomposites were synthesized by a two-phase solvothermal method by adjusting the pH value to 2.0. Affected by the size of nanoparticles, the nanocomposites with MoO$_2$ nanoparticles (100 nm) uniformly anchored on the RGO nanosheets exhibit a more superior electrochemical performance with a high capacity of 765.1 mAh g$^{-1}$ after 50 cycles, which is expected to be a promising anode material for lithium-ion batteries.

Keywords. MoO$_2$/RGO; Lithium-ion battery; Anodes.

1. Introduction

As a portable energy storage instrument, lithiumion batteries (LIBS) have been extensively concerned and applied widely [1]. However, the low theoretical capacity (TC: 372 mAh g$^{-1}$) of traditional graphite anode material is not sufficient to meet the practical application [2]. In this regard, further research is still needed to develop new anode electrode materials with high performance. For the reason of high TC and power density, transition metal oxides (TMOs) have been supposed to be an anode material candidate. As we all know, the size of the TMOs is crucial in the process of lithium insertion when served as an anode material. Nanoscale anode materials can realize higher intercalation/deintercalation rates to boost power energy because of the larger surface area and fast electron transport. Among the various nanoscale TMOs, MoO$_2$ is regarded as a promising anode material, resulting from its relative high TC (838 mAh g$^{-1}$) and excellent chemical stability. However, the poor conductivity and large volume changes in the process of charge and discharge seriously place restrictions on its use in LIBs. Reduced graphene oxide (RGO) is a popular substrate owing to the large specific surface area, excellent conductivity, and superb chemical stability, which has drawn much attention in many fields. Meanwhile, the TMOs can be fixed on the surface of graphene by the remnant oxygen-containing functional groups of graphene, which can efficiently alleviate the agglomeration of nanoparticles. Therefore it is a promising strategy by compositing TMOs with RGO to improve the conductivity, and reduce the capacity attenuation caused by volume variation [3, 4].

In this work, MoO$_2$/RGO nanocomposites were fabricated via a two-phase solvothermal reaction. The adjustment of pH value is crucial in controlling the size of MoO$_2$ supported on the surface of RGO. MoO$_2$/RGO nanocomposites display excellent lithium storage performance with a high discharge...
capacity of 765.1 mAh g\(^{-1}\) and excellent stability at 100 mA g\(^{-1}\).

2. Experimental

2.1. Synthesis of MoO\(_2\)/RGO Nanocomposites

GO solution with 5.5 mg/mL was synthesized through a pressurized oxidation and multiplex reduction method \[5\]. Solution A was first prepared through dissolving 1 g Na\(_2\)MoO\(_4\)•2H\(_2\)O in 10 mL GO solution. Solution B was prepared by dissolving 3 g oleylamine in ethanol (20 mL) and hexane (30 mL) mixed solution. Subsequently, mixed the above two solutions under continuous magnetic stirring with adjusting pH values 1.5, 2.0, and 2.5 by 6 M HCl, respectively. After a stirring process for 30 min, the mixture was transferred to a autoclave with a volum of 100 mL, and react at 200 °C for 24 h. After that, the upper was collected, and washed by ethanol and n-hexane. Conclusively, the production was annealed at 400 °C for 3 h under argon condition, and marked as “Sample A, B, C,” respectively, with corresponding pH values of 1.5, 2.0, and 2.5.

![Figure 1](image.png)

**Figure 1.** (a) XRD patterns, (b) FT-IR spectra, (c) Raman spectra of samples A, B, and C. TEM images of (d) Sample A, (e) Sample B, and (f) Sample C.

2.2. Electrochemical Measurements

The MoO\(_2\)/RGO anode was prepared by mixing the active material (80%), acetylene black (10%), PVDF (10%) with NMP to form a slurry, then coated it onto Cu foil. The detailed testing process is the same as the literature \[6\].

3. Results and Discussion

Figure 1a illustrate the monoclinic MoO\(_2\) (JCPDS No. 78-1070) of the as-prepared samples. The peaks at 26.19°, 36.88°, 53.71°, and 60.89°, are assigned to the (011), (-211), (022), and (031) planes of monoclinic MoO\(_2\), respectively. In the FT-IR spectrum (Figure 1b) of GO, the wavenumbers at 3400, 1731, 1627, 1220, and 1050 cm\(^{-1}\), correspond to hydroxyl, carbonyl, carboxyl, epoxy, and C–O groups of GO. After hydrothermal process, the decreased C-O-C group at 865 cm\(^{-1}\) and appeared C=C peak at 1550 cm\(^{-1}\) suggest the GO has been successfully reduced to RGO in the composite. Raman spectra can further characterize the structure of the as-prepared samples (Figure 1c). Five peaks at 992, 818, 662, 335 and 282 cm\(^{-1}\) are corresponded to the typical peaks of MoO\(_2\). The peaks at 1344 and 1586 cm\(^{-1}\) ascribed to D-band and G-band for RGO in MoO\(_2\)/RGO nanocomposites demonstrate the low graphitization degree of the RGO. Transmission electron microscopy (TEM) was employed for exploring the particulate shapes of the three kinds of MoO\(_2\)/RGO nanocomposites. When the pH value was adjusted to 1.5, MoO\(_2\) nanoparticles beyond 10 nm in size are uniformly loaded on the RGO nanosheets (Figure 1d). Meanwhile, some agglomerations of nanoparticles occurred. When the pH value was adjusted to 2.0, MoO\(_2\) nanoparticles are uniformly dispersed in the nanosheets without obvious agglomeration (Figure 1e). When the pH value increases to 2.5, the size of MoO\(_2\) nanoparticles grows...
XPS spectra (Figure 2a) were further used to confirm the surface elements of Sample B. Mo, O, C elements exist in MoO$_2$/RGO. In Figure 2b, the peaks of Mo 3d region at 229.6 and 232.9 eV are corresponded to Mo$^{4+}$ 3d$_{5/2}$ and 3d$_{3/2}$. Meanwhile, the peak at 231.6 eV (235.9 eV) is attributed to Mo$^{6+}$ 3d$_{5/2}$ (3d$_{3/2}$), due to the slight oxidation in the air [7, 8]. In Figure 2c, the peaks are belonged to O–C–O (288.8 eV), C=O (286.7 eV), C–O (285.2 eV), and C–C (284.6 eV), respectively. The spectrum of O 1s in Figure 2d shows the lattice oxygen of MoO$_2$ at 530.7 eV, and the oxygen-containing functional group of graphene at 532.4 eV.

![Figure 2](image_url)

**Figure 2.** (a) Survey XPS spectra of Sample B; (b) High-resolution XPS spectra of Mo 3d, (c) C 1s, and (d) O 1s.

Figure 3 displays the charge-discharge (CD) curves of the MoO$_2$/RGO nanocomposites in the first three cycles. For the three sample of A, B, and C, the initial specific discharge capacities are 624, 670, and 552.1 mAh g$^{-1}$, individually, suggesting high performance of MoO$_2$/RGO nanocomposite. And the first specific charge capacities are 479.6, 576.2, and 505.3 mAh g$^{-1}$, separately. The loss of capacity during the first CD may be due to the process of electrolyte decomposition or the solid electrolyte interface (SEI) formation [9]. During the first cycle, two CD platforms appear at 1.55/1.25V and 1.47/1.73 is resulting from phase transition from monoclinic to orthorhombic during the intercalation and de-intercalation process of LIB [10, 11], which can be represented by the following equations:

\[
x \text{Li}^{+} + x \text{e}^{-} + \text{MoO}_2 \leftrightarrow \text{Li}_x\text{MoO}_2 \quad (0 < x < 0.98) \quad (1)
\]

\[
\text{Li}_0.98\text{MoO}_2 + 3.02 \text{Li} \leftrightarrow 2 \text{Li}_2\text{O} + \text{Mo} \quad (2).
\]
Figure 4. (a) Cycling performance of MoO$_2$/RGO electrodes at 100 mA g$^{-1}$; (b) Rate capacity of MoO$_2$/RGO electrodes at various current densities. Cyclic voltammograms (CVs) of the MoO$_2$/RGO electrodes at a scan rate of 0.1 mV s$^{-1}$ for the first three cycles: (c) Sample A, (d) Sample B, (e) Sample C. (f) Electrochemical impedance spectra of the MoO$_2$/RGO and MoO$_2$ electrodes.

The Cycling performance of Sample B is superior to those of Sample A and C with the discharge/charge capacity at 100 mA g$^{-1}$ remaining 765.1 mA h g$^{-1}$ after 50 cycles (Figure 4a). Rate capacity of MoO$_2$/RGO is displayed in Figure 4b. The capacity still remains ~ 700 mA h g$^{-1}$ even at 1000 mA g$^{-1}$. While, the capacity rises again to ~ 850 mA h g$^{-1}$ after the current density returns back to 100 mA g$^{-1}$, indicating the superior rate capabilities of Sample B. As shown Figure 4c-e, the CV curves show two obvious pairs redox peaks appear at 1.25/1.55 V and 1.47/1.73 V during the CD process, suggesting the phase transition of the monoclinic to the orthorhombic, which is consistent with the results of charge-discharge voltage profiles. The Nyquist plots for the pristine MoO$_2$ and MoO$_2$/RGO are displayed in Figure 4f. In the high frequency region, the semicircle radius of MoO$_2$/RGO is smaller than the MoO$_2$, indicating that MoO$_2$/RGO has a lower charge transfer resistance.

4. Conclusion

In conclusion, MoO$_2$/RGO nanocomposites were prepared by a two-phase solvothermal method via adjusting the pH value to 2.0. Electrochemical studies show that MoO$_2$/RGO nanocomposites display superior reversible capacity and rate capacity. After 50 cycles, the capacity of MoO$_2$/RGO can still maintain 765.1 mA h g$^{-1}$ at 100 mA g$^{-1}$. Therefore, MoO$_2$/RGO nanocomposites has great development for practical lithium-ion batteries.

References

[1] Huang X, Sun J, Wang L, Tong X, Dou S, Wang Z, 2021 Small 2004369.
[2] Xu H, Zhang Y, Song X, Kong X, Ma T, Wang H, 2020 J. Alloys Compd. 153289.
[3] Zhang X, Fu C, Li J, Yao C, Lu T, Pan Li, 2017 Ceram. Int. 43 3769-3773.
[4] Yin J, Sun P, Qu G, Xiang G, Hou P, Xu X, 2020 Appl. Surf. Sci. 508 144698.
[5] Bao C, Song L, Xing W, Yuan B, Wilkie C, Huang J, Guo Y, Hu Y, 2012 J. Mater. Chem. A 22 6088-6096.
[6] Geng Q, Tong X, Wenya G, Yang C, Wang J, Maloletnev A, Wang Z, Su X, 2018 Nanoscale Res. Lett. 13 129.
[7] Liu S, Li F, Wang D, Hang C, Zhao Y, Baek J, Xu J, 2018 Small Methods 2, 1800040.
[8] Zhao C, Song H, Zhuang Q, Ma Q, Liang J, Peng H, Mao C, Zhang Z, Li G, 2018 Inorg. Chem. Front. 5, 1026-1032.
[9] Wang B, Yuan F, Li W, Wang Q, Ma X, Gu L, Sun H, Xi K, Zhang Di, Wang W, 2020 Nano Energy 75 104979.
[10] Xu G, Liu P, Ren Y, Huang X, Peng Z, Tang Y, Wang H, 2017 J. Power Sources 361 1-8.
[11] Zhou E, Wang C, Shao M, Deng X, Xu J, 2017 Ceram. Int. 43 760-765.