Synthesis and Electrochemical Performance of TiO$_2$/rGO Composites with Different Layers of Graphene Oxide as Anode Materials for Lithium-ion Battery

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Abstract. The lithium-ion battery anode materials TiO$_2$/rGO were synthesized from different layers of graphene oxide (GO) and Titanium oxysulfate using hydrothermal method. The structure and morphology were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Their electrochemical performances were tested through galvanostatic charge/discharge and electrochemical impedance spectrum (EIS). The test results show that the TiO$_2$/rGO (few-layers) composites exhibited better electrochemical performance than the TiO$_2$/rGO (multi-layers) composites. At the current density of 100 mA/g, the discharge capacity of TiO$_2$/rGO (few-layers) is 285.3 mAh/g after 100 cycles, and the Coulombic efficiency is still maintained as high as 98.6%, which is superior to that of the TiO$_2$/rGO (multi-layers). TiO$_2$/rGO (few-layers) electrode shows good rate capability and enhanced electrochemical performance compared with the TiO$_2$/rGO (multi-layers) electrode.

1. Introduction
With the rapid development of economy worldwide, environmental pollution and energy crisis have been severely accumulated due to the excessive utilization of fossil fuel resource. Therefore, developing clean and sustainable energy resources has attracted more and more attention. Due to its high energy density, high operating voltage, long cycle life and environmental friendly, Lithium-ion batteries (LIBs) is considered to be an ideal energy storage and conversion device [1-3]. Among the main components in LIBs, such as electrodes, electrolytes, and separator, the selection of electrode materials is very important in enhancing LIBs’ performance. Therefore, the development of electrode materials with higher capacity and better rate performance has become the hot topic.

In recent years, as a new type of anode materials, metal oxides have been widely investigated as anode materials for LIBs owing to their higher theoretical specific capacity than the traditional commercial graphite anode [4]. In this respect, TiO$_2$ has attracted huge attention because of its abundance, low cost and environmental benignity [5]. In addition, compared to other metal oxides, such as SiO$_2$, SnO$_2$, and MgO, the massive volume changes during the charge-discharge processes can damage the anodes gradually and further cause electrical short circuit and the drastic decrease of cycle life [6, 7]; however, TiO$_2$ has lower volume variation (<4 %) during the lithiation/delithiation process which favors large-scale energy storage. Unfortunately, TiO$_2$ has poor electronic and ionic conductivity that limits its application as a high power anode material [8]. In order to overcome the shortcoming, several studies focusing on the composites formation of TiO$_2$ with graphene have been investigated [9, 10]. However, researchers did not conduct further study on the influence of the layers of graphene on TiO$_2$/graphene composites, and the prepared graphene includes the single layer, the few layers and multi layers, which is a mixed layer for GR, ignoring the influence of graphene layers
on composites [11-13]. There is no specific investigation about the influence of graphene layers on composite materials.

Herein, to make up the pity for the researches, we present a facile hydrothermal method to synthesize TiO$_2$ nanoparticles dispersed on rGO layers by using Titanium oxysulfate and graphene oxide(GO) as the precursor in the synthesis system. Different from the previous methods, we used few-layers GO (1-5) and multi-layers GO (5-10) as raw material, exploring the influence of the graphene layers on the electrochemical performance of composites.

2. Experimental

TiO$_2$/rGO nanocomposites were synthesized by hydrothermal method. In the process, hydrazine hydrate as the reducing agent was introduced into the reaction. In a typical synthesis, 60 mg multi-layers GO were ultrasonically dispersed in the 60 mL distilled water. Moreover, 391.8 mg Titanium oxysulfate were dissolved into the 20 mL ethyl alcohol under the magnetic stirring, and then the solution was added into the GO. After stirring for 30 min, the hydrazine hydrate was slowly added to above mixed solution; the reaction solution was transferred in an autoclave and kept at 150 °C for 14 h. After cooling and centrifugation, washing was carried out with ethyl alcohol and distilled water for several times. Then dried in the air at 80°C for 24 h to obtain the desired TiO$_2$/rGO (multi-layers) composites. On the other hand, TiO$_2$/rGO (few-layers) composites was synthesized under the same experimental conditions for comparison.

The structure of the as-prepared TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites was examined by X-ray powder diffraction (XRD; MiniFlex600, Rigaku Corporation, Japan, CuKa radiation) with the 2θ range used in the measurement was from 10° to 80°. Their morphology and component were characterized by scanning electron microscope (SEM; SU8010, Japan) with an energy dispersive spectrometer (EDS) and Fourier transfer infrared spectroscope (FTIR; IRPrestige-21/FTIR-8400s).

The working electrode was fabricated by well-dispersed slurry, which contained the active material (TiO$_2$/rGO), acetylene black and polyvinylidene fluoride (PVDF) binder at the weight ratio of 70:20:10 in N-methyl-2-pyrrolidinone (NMP). After the above slurry was coated on Cu foils, and drying in a vacuum oven at 110 °C for overnight. The cells used these active materials as the working electrode, highly pure lithium was used as the counter electrode and reference electrode. The CR2032 coin-type cells for evaluating electrochemical performances were assembled in a glove box of argon atmosphere. The galvanostatically charged-discharged was tested for a potential range of 0.01-3.0 V using the Land Battery Test System (CT2001A, Wuhan Land Corporation, China). Electrochemical impedance spectra (EIS) of TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) after 100 cycles were tested at the electrochemical workstation (CHI660; CH Instruments, Shanghai Chenhua Instrument Corporation, China) in the frequency range from 10 mHz to 100 kHz [14].

3. Results and Discussion

3.1. Structure and Morphology of Materials

The XRD patterns of graphene oxide (GO), commercial graphene (GR), TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites are shown in figure 1, indicating that all the strong diffraction peaks observed with TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites both are attributed to the typical anatase TiO$_2$ phase (JCPDS No.21-1272, Space group: I41/amd). The intense diffraction peaks at 2θ=25.7°, 37.5°, 48.8°, 54.8°, 55.9°, 63.1°, 69.9°, 71.5° and 75.4° can be perfectly indexed as the (101), (103), (200), (105), (211), (213), (116), (220), (107) plane of the standard anatase TiO$_2$ phase, respectively, indicating that crystalline TiO$_2$ could be formed by the hydrothermal reaction. There is no obvious diffraction assigned to GO in the as-prepared TiO$_2$/rGO composites, indicating the reduction of graphene oxide (GO) in the reaction. In addition, it should be mentioned that there is no obvious observation of the (002) diffraction peak for graphene in as-prepared composites, because the quantity of graphene is minute and the diffraction peak of TiO$_2$ (101) is exceedingly close to the peak of graphene (002).
Figure 1. XRD patterns of materials.

Figure 2. FTIR spectra of materials

Figure 2 shows the Fourier transform infrared spectroscopy (FTIR) spectra of GO, TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites. There are some oxygen-containing functional groups, such as O-H stretch at 3415 cm$^{-1}$, C=O stretch at 1725 cm$^{-1}$, C-O stretch at 1204 cm$^{-1}$ and 1039 cm$^{-1}$ in the GO [15,16]; however, these stretches were weakened or disappeared in the TiO$_2$/rGO composites, indicating the successful reduction of GO to graphene during the hydrothermal process. This result is agreement with the XRD patterns. In addition, the stretching vibration characteristic peak of C=C at about 1590 cm$^{-1}$ still exists for composites, and the absorption signals in the range of 500-700 cm$^{-1}$ should be assigned to the Ti-O stretching vibration peak [17], indicating that the structure of graphene was not destroyed during the hydrothermal reaction, and TiO$_2$ was successfully prepared.

The morphology and structure of the composites were also observed by the SEM images. As seen in figure 3, stacks of overlapping graphene layers with folds and wrinkles are characteristics of graphene. As shown in figure 3c, the TiO$_2$ nanoparticles aggregate into large particles. The resulting large particles would lead to the poor rate performance as anode material due to the long diffusion path of electron and Li$^+$ transport. Compared with TiO$_2$/rGO (multi-layers) composites, it was found that the particle dispersion of TiO$_2$/rGO (few-layers) composites was significantly better than that of the TiO$_2$/rGO (multi-layers).

Figure 3. SEM images of materials: (a) GO (multi-layers), (b) GO (few-layers), (c) TiO$_2$/rGO (multi-layers), (d) TiO$_2$/rGO (few-layers).

EDS is used to determine the component of the as-prepared product. Figure 4 demonstrates the EDS spectra of materials, and the elements content are listed in table 1 and table 2. It can be seen that
multi-layers GO and few-layers GO are composed of C and O elements with a ratio of 2:1. EDS analysis (figure 4c and figure 4d) confirms the presence of C, O, and Ti elements in the composites, suggesting the atomic ratio of TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) are around 4:2:1. According to the relative atomic mass of each element, rGO and TiO$_2$ contents after hydrothermal reduction estimated from EDS analysis are found to be about 4:5. The oxygen (O) element mainly has two sources. On the one hand, one Ti atom in TiO$_2$ introduces two O atoms, and on the other hand, few non-reduced oxygen-containing functional groups still exist in the structure of graphene. It is worth noting that the content of O atoms in TiO$_2$/rGO (multi-layers) composites is more than that of the TiO$_2$/rGO (few-layers) composites, which indicates that the hydrothermal reduction reaction of TiO$_2$/rGO (multi-layers) is not complete compared with TiO$_2$/rGO (few-layers) composites. Combined with SEM, we can see that although few particles of TiO$_2$/rGO (few-layers) composites are dispersed on the graphene layers, the number of Ti atoms is slightly more than TiO$_2$/rGO (multi-layers) composites, which further proves that many particles in TiO$_2$/rGO (few-layers) are embedded in the layers of graphene, displaying a good dispersion of nanoparticles on graphene. When the particles are embedded inside the material, it is beneficial to the contact between the electrolyte and the materials, and further improving the electrochemical performance of the material.

![Figure 4. EDS spectra of materials: (a) GO (multi-layers), (b) GO (few-layers), (c) TiO$_2$/rGO (multi-layers), (d) TiO$_2$/rGO (few-layers).](image)

**Table 1.** The elements ratio of GO.

| Element | GO (multi-layers) | GO (few-layers) |
|---------|-------------------|-----------------|
|         | Weight (%)        | Atomic (%)      | Weight (%)        | Atomic (%)      |
| C       | 59.85             | 66.50           | 60.59             | 67.19           |
| O       | 40.15             | 33.50           | 39.41             | 32.81           |

**Table 2.** The elements ratio of composites.

| Element | TiO$_2$/rGO (multi-layers) | TiO$_2$/rGO (few-layers) |
|---------|---------------------------|--------------------------|
|         | Weight (%)                | Atomic (%)               | Weight (%)                | Atomic (%)               |
| C       | 37.37                     | 59.93                    | 39.07                     | 60.92                    |
| O       | 31.89                     | 28.20                    | 29.41                     | 26.38                    |
| Ti      | 30.74                     | 11.87                    | 31.52                     | 12.70                    |
3.2. Electrochemical Performance

Figure 5 shows typical charge-discharge curves of the TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites in the 1st, 2nd, 10th, 50th, and 100th cycle at the current density of 100 mA/g, respectively. As can be seen from the figure 5, a feature of interest is that the first discharge curve of the two composites can be divided into three regions: 1) it can be seen that the voltage decreases monotonically from 3.0 to 1.7 V, corresponding to the internal activation process of the battery because of the applied current, and which is a common phenomenon; 2) the first discharge curve for TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites show an obvious plateau at about 1.7 V corresponds to the lithium storage reaction into the lattice of anatase TiO$_2$, which is the typical characteristic of anatase TiO$_2$ electrodes \[18\]; 3) along with the first discharge in LIBs test, the plateau at about 1.7 V disappeared gradually. While the plateau decreases to about 0.85 V for the TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) electrodes during the first discharge process, corresponding to the formation of the solid electrolyte interphase (SEI) during the first discharge. After that, the curve slowly drops to the discharge cut-off voltage.

![Charge-discharge curves](image)

**Figure 5.** Charge-discharge curves of composites at the current density of 100 mA/g.

From the second cycle, the discharge plateau at about 1.7 V corresponds to the lithium storage reaction into the anatase TiO$_2$, and the charge plateau at about 2.0 V is related to the lithium extraction from TiO$_2$; with the more cycles for test, the charge plateau at about 2.0 V moves to about 2.1 V, which is basically the same as the trend of the charge-discharge curve of anatase TiO$_2$ \[19\]. In addition, the large initial capacity loss can be attributed to irreversible processes for instance the formation of SEI film during the first discharge, which is common in most anode materials. On the other hand, the first discharge specific capacity of TiO$_2$/rGO (few-layers) composites (1390.7 mAh/g) was found to be higher than that of the TiO$_2$/rGO (multi-layers) composites (1067.2 mAh/g).

![Cycle performances](image)

**Figure 6.** Cycle performances of composites at the current density of 100 mA/g.
Cycling performance of the electrode materials is important for its application. Figure 6 shows the cycling performance of TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) electrodes at the current density of 100 mA/g. After 100 cycles, the discharge specific capacity of TiO$_2$/rGO (multi-layers) was 236.6 mAh/g, and the Coulombic efficiency was 98.5%; TiO$_2$/rGO (few-layers) delivered 285.3 mAh/g and 98.6%, respectively. Comparing the TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers), it was found that the composites prepared by using the few-layers of graphene oxide as a precursor had better cycle stability and higher specific capacity.

The rate capability of composites electrode was evaluated stepwise by increasing the galvanostatic current from 10 mA/g to 320 mA/g (10, 20, 40, 80, 160, 320 mA/g), then returning to 10 mA/g. As can be seen from figure 7, although the specific capacities were decreased along with the increase of current density from 10 mA/g to 320 mA/g, remaining relatively stable at each stage. At the higher current density of 160 mA/g and 320 mA/g, the discharge capacities of each period for TiO$_2$/rGO (few-layers) are 201.2 mAh/g and 162.5 mAh/g, respectively; however, the discharge capacities of TiO$_2$/rGO (multi-layers) are only 78.9 mAh/g and 49.6 mAh/g, respectively. In addition, after the high current density measurements, the specific capacity of the composites almost recovers to the initial value, indicating excellent cycling stability. At the same time, the TiO$_2$/rGO (few-layers) electrode exhibited better rate performance than the TiO$_2$/rGO (multi-layers) at all the current densities. These results indicate that the TiO$_2$/rGO (few-layers) electrode have excellent cycling and rate performances.

Figure 7. The rate performance of materials

Figure 8. Impedance spectra of composites

Figure 8 demonstrates the electrochemical impedance spectra (EIS) of the TiO$_2$/rGO (multi-layers) and TiO$_2$/rGO (few-layers) composites, which were investigated in the discharge state after 100 cycles. The EIS can be explained by an equivalent circuit, which is shown in the insert of figure 8. It can be seen from the figure 8 that the impedance spectras of the materials are composed of two semicircles in the high and intermediate frequency region, a sloping line in the low frequency region. The two semicircles result from the SEI film ($R_{SEI}$) and the charge transfer reaction ($R_{ct}$), the sloping line is related to the diffusion of Li into the active materials ($W$) [20]. The fitted impedance parameters of the equivalent circuit are listed in table 3. The TiO$_2$/rGO (few-layers) composites electrode has the lower charge transfer resistance, and the conductivity is significantly better than TiO$_2$/rGO (multi-layers). In the process of hydrothermal synthesis, TiO$_2$ exhibited better dispersibility on the few-layers graphene, which is beneficial to the transmission diffusion of Li$^+$, and indicating that the few-layers graphene is more suitable for anode materials of lithium battery.

Table 3. The fitted parameters in the impedance spectroscopy

| Material              | $R_S$/Ω | $R_{SEI}$/Ω | $R_{ct}$/Ω |
|-----------------------|---------|-------------|------------|
| TiO$_2$/rGO(multi-layers) | 5.08    | 67.81       | 77.59      |
| TiO$_2$/rGO(few-layers) | 3.34    | 31.91       | 69.74      |
4. Conclusions

(1) TiO$_2$/GO composites were successfully prepared by hydrothermal method using different layers of graphene oxide and Titanium oxysulfate as the precursor. The XRD and FTIR results showed that the GO was successfully reduced to graphene, and the obtained TiO$_2$ was anatase; SEM images revealed that TiO$_2$ had better dispersibility in the TiO$_2$/rGO (few-layers) composites.

(2) After 100 charge-discharge cycles, the discharge specific capacity of TiO$_2$/rGO (multi-layers) was 236.6 mAh/g, and the Coulombic efficiency was 98.5%; the discharge specific capacity of TiO$_2$/rGO (few-layers) composites can still be maintained at 285.3 mAh/g, and the Coulombic efficiency was 99.6%, which was higher than that of the TiO$_2$/rGO (multi-layers) composites.

(3) TiO$_2$/rGO (few-layers) composites exhibited better rate performance than the TiO$_2$/rGO (multi-layer) composites. In addition, the SEI film resistance and charge transfer resistance of TiO$_2$/rGO (few-layers) composites were lower, which is favorable for the electrochemical performance of the material.

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6. References

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