A Facile Approach for Preparing MnO₂-Graphene Composite as Anode Material for Lithium-Ion Batteries

Kang Wen¹, Guanghui Chen², Feng Jiang¹, Xiangyang Zhou²*, Juan Yang²

¹ School of Materials Science and Engineering, Central South University, Changsha 410083, China
² School of Metallurgy and Environment, Central South University, Changsha 410083, China
*E-mail: hncsyjy308@163.com

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A facile method to prepare the MnO₂-graphene composite was proposed. The composite with a sandwich structure was synthesized by oxidizing part of the carbon atoms in the framework of graphene. By using graphene as buffer carrier, MnO₂ was homogeneously coated onto the surface of graphene. Electrochemical properties of this MnO₂-graphene composite were characterized and it exhibits excellent cyclic stability and good rate properties. The MnO₂-graphene electrode retains a capacity of 752 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 65 cycles, making it a promising anode material for lithium ion batteries.

Keywords: MnO₂, graphene, composite, lithium ion batteries, oxidation

1. INTRODUCTION

Due to the depletion of fossil fuels and increasing environmental problems, great efforts have been made to develop novel electrochemical systems for energy storage and conversion [1, 2]. Lithium ion batteries (LIBs) are considered to be one of the most practical and effective technologies for energy storage and conversion [3, 4]. Therefore, developing the next generation LIBs with high energy density, high power density and excellent cycling performance becomes critical [5]. In the last several years, great efforts have been made to develop new electrode materials to satisfy these demands [3, 6], and MnO₂ was considered to be a promising electrode material for LIBs due to its high theoretical capacity (1230mAh g⁻¹), low cost, environmental friendliness and natural abundance [7-9]. However, the low actual capacity and the poor cyclability of MnO₂ due to its large volume expansion and aggregation during Li insertion/extraction hindered its practical application [10-12]. As is well-known,
an effective way to solve these problems is to fabricate hybrid electrode materials that incorporated \( \text{MnO}_2 \) onto electrically conductive carbon materials [13, 14] or conducting polymers [15-17].

Graphene, a two-dimensional carbon material, is an ideal matrix for growing and anchoring nanomaterials for energy storage due to its superior electrical conductivity, high surface-to-volume ratio, ultrathin thickness, structural flexibility, and chemical stability [18, 19]. In recent reports, the \( \text{MnO}_2 \)/graphene nanocomposites used as electrode materials for supercapacitors have been synthesized by using different methods [20-22]. In this work, a unique hierarchical structure was designed and the \( \text{MnO}_2 \)/graphene composite was synthesized by oxidizing part of the carbon atoms in the framework of graphene.

A facile approach for preparing the \( \text{MnO}_2 \)/graphene composite was presented in this paper. The \( \text{MnO}_2 \)/graphene composite exhibited a sandwiched structure, and \( \text{MnO}_2 \) were well anchored onto the surface of graphene and incorporated between the layers. Meanwhile, as anode materials for lithium ion batteries, electrochemical performances of the \( \text{MnO}_2 \)/graphene composite were characterized by cyclic voltammetry (CV) and galvanostatic charge-discharge tests.

2. EXPERIMENTAL

2.1 Synthesis of pure \( \text{MnO}_2 \) and \( \text{MnO}_2 \)/graphene composite

Graphite oxide was prepared by Hummers method [23]. The as-prepared graphite oxide suspension was then dispersed in water to create a 0.05 wt.% dispersion. Exfoliation of graphite oxide to graphene oxide (GO) was achieved by ultrasonication of the dispersion for 120 min. The obtained brown dispersion was then subjected to 30 min of centrifugation at 3000 rpm to remove unexfoliated graphite oxide. In a typical procedure for chemical conversion of graphite oxide to graphene, the resulting homogeneous dispersion (200ml) was mixed with a given amount of hydrazine solution and 1.4 ml of ammonia solution (28 wt.% in water) in a 250 ml conical flask. The mass ratio of hydrazine to GO was about 7:10. After being vigorously stirred for a few minutes, the flask was then put in a water bath (95°C) for 1 h [24].

The procedure for synthesizing the \( \text{MnO}_2 \)/graphene composite was illustrated in Fig.1. First, 300 mg \( \text{KMnO}_4 \) was added into the above suspension and the mixed solution was stirred with a stirring bar for 3h at 80°C. In this process, nanocrystalline \( \text{MnO}_2 \) formed on the surface of graphene framework due to the redox reaction [25, 26] shown as follows:

\[
4\text{KMnO}_4 + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{K}_2\text{CO}_3 + 2\text{KHCO}_3
\]  

(1)

After this, the produced sample was collected by filtration and should be washed several times with deionized water. The final \( \text{MnO}_2 \)/graphene product was dried at 80 °C in a vacuum oven for 12 h.

For the preparation of \( \text{MnO}_2 \) powders, 300mg \( \text{KMnO}_4 \) and 0.2 ml \( \text{H}_2\text{SO}_4 \) (95%) was mixed with 25ml deionized water to form precursor. Then the precursor solution was transferred into a Teflon-sealed autoclave to carry out hydrothermal treatment at 150°C for 4h [27].
2.2 Characterization

Raman spectra of samples were recorded on a LabRAM HR800 spectrometer. Phases in MnO₂-graphene composite were identified by using X-ray powder diffraction (XRD, Rigaku-TTRIII with Cu Kα radiation). The morphologies of as-obtained samples were observed on a scanning electron microscopy (SEM, JSM-6360LV) and transmission electron microscope (TEM, JEM-2100). The content of interlayer water and MnO₂ in the composite was determined by adopting thermogravimetric analysis (TGA, SDTQ 600).

2.3 Electrochemical measurement

The test electrodes consisted of the active materials (80 wt.%), acetylene black (10 wt.%) and polyvinilidene difuoride (10 wt.%). The mixture was dissolved in N-methyl-2-pyrrolidene (NMP) under stirring to form slurry. Then the slurry was coated onto a copper foil substrate and dried in a vacuum oven for 12h at 120°C. Electrochemical tests were performed using CR2025 coin-type cells with lithium metal foils as the counter electrode. A solution of 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (volume ratio of EC:DMC was 1:1) was used as the electrolyte, and the separator was Polypropylene membrane (Celgard-2400). The cells were charged and discharged under constant current within the voltage range from 0.01 to 3 V vs. Li/Li⁺ on LAND batteries tester (CT-2001A, Wuhan Jinnuo Electron Co. Ltd.). Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CHI660, China).

3. RESULTS AND DISCUSSION

Figure 2 shows a typical XRD pattern of the as-prepared MnO₂-graphene composite. Apart from the peaks of graphene, three broad peaks centered at 12°, 37°, and 66° are observed. These peaks can be indexed to α-MnO₂ (JCPDS file no. 42–1169), including its amorphous phase.
Raman spectroscopy is useful for analyzing the structure of inorganic materials with poor crystallinity [2]. As shown in Figure 3, two obvious peaks can be observed at 1590 cm\(^{-1}\) and 1350 cm\(^{-1}\) in the Raman spectrum of graphene, and this can be assigned to the G and D bands of graphene [28]. In Raman spectra of pure MnO\(_2\) and MnO\(_2\)-graphene composite, the peaks at around 640 cm\(^{-1}\) are in good agreement with the Raman feature of birnessite-type MnO\(_2\) compounds reported before [29], which can be viewed as the symmetric stretching vibration (Mn-O) of the MnO\(_6\) groups [30]. In the Raman spectrum of MnO\(_2\)-graphene composite, the intensity of graphene peaks decreased as the reaction described in equation (1) occurred, indicating the replacement of carbon atoms by MnO\(_2\) in the framework of graphene.

![Figure 2. XRD pattern of the MnO\(_2\)-graphene composite](image)

![Figure 3. Raman spectra of (1) graphene, (2) MnO\(_2\), and (3) MnO\(_2\)-graphene composite](image)

TGA curves of the as-prepared MnO\(_2\)-graphene composite is shown in Figure 4. The MnO\(_2\)-graphene composite exhibits obvious weight loss from 25 to 1000 °C. The 16.6 % weight loss between 25 and 150 °C could be attributed to the liberation of adsorbed water in composites. An additional 37%
weight loss between 300 and 450 °C corresponds to the loss of graphene [27]. Therefore, the content of MnO$_2$ in the MnO$_2$-graphene composite is 46.4%.

![TGA curve of the MnO$_2$-graphene composite](image)

**Figure 4.** TGA curve of the MnO$_2$-graphene composite

Figure 5a shows the typical morphology of the MnO$_2$-graphene composite. It can be seen that MnO$_2$ particles existed on the surface of graphene, and the composites exhibit clear lamellar structure. The large surface area of graphene enabled sufficient interaction between MnO$_2$ nanoparticles and graphene, facilitating the formation of sandwich structures. Figure 5b is the TEM image of MnO$_2$-graphene composite. It can be seen that the MnO$_2$ nanoparticles was attached on the surface of graphene or sandwiched between the layers, and the graphene served as supporter and electrically medium [31]. The surface of graphene was decorated randomly with MnO$_2$ nanoparticles. The excellent flexibility of graphene and the sandwich structure of this composite could effectively buffer the volume expansion of MnO$_2$ during the charge/discharge process. In addition, graphene in the composite act as not only lithium storage electrode but also good conductive medium to facilitate the electron transportation. Large surface areas of graphene sheets and MnO$_2$ nanoparticles provide sufficient areas for interactions between electrode and electrolyte. Moreover, MnO$_2$ nanoparticles on the surfaces of graphene could also prevent the stack of graphene sheets. In summary, due to the synergistic effects of MnO$_2$ nanoparticles and graphene, this composite exhibited high electrical conductivity and excellent electrochemical performance.

![SEM and TEM images of MnO$_2$-graphene composite](image)

**Figure 5.** (a) SEM and (b) TEM images of MnO$_2$-graphene composite
Figure 6 shows the cyclic voltammetry curves and the first three galvanostatic charge-discharge profiles of MnO$_2$-graphene composite electrode between 0.01 V and 3 V at a scanning rate of 1 mV s$^{-1}$. The CV curves presented in Figure 6a clearly showed the redox peaks corresponding to the intercalation and deintercalation of Li ions into/from the MnO$_2$-graphene electrode. During the first negative scan, a cathodic peak appeared at 0.55 V, corresponding to the formation of a solid electrolyte interphase (SEI) layer. This peak disappeared after the first cycle, demonstrating that the SEI formation mainly occurs in the first cycle. Two oxidation peaks at 1.3 V and 2.1 V can also be observed in the curves, indicating the two-step electrochemical oxidation of Mn$^0$ to Mn$^{4+}$. In agreement with the CV results, two voltage plateaus can be observed during the charge process. However, there was only one plateau in the discharge process, demonstrating the reduction reaction of MnO$_2$ with Li ions in one step. The reaction between MnO$_2$ and Li can be described as follows [32, 33]:

\[
\text{MnO}_2 + 4\text{Li} + 4e^- \rightleftharpoons 2\text{Li}_2\text{O} + \text{Mn}
\]  

(2)

Figure 6. (a) Cyclic voltammetry curves and (b) the first three charge-discharge profiles of MnO$_2$-graphene electrode between 0.01 V and 3 V at a current density of 100 mA g$^{-1}$.

The first discharge and charge capacities are 1589 and 746 mAh g$^{-1}$, respectively, with a coulombic efficiency of 47%. It should be noted that the discharge capacity for the first cycle of MnO$_2$-graphene electrode is much higher than the theoretical value of pure MnO$_2$ (1230 mAh g$^{-1}$). This could be attributed to the irreversible reactions of electrodes, i.e. the formation of solid electrolyte interphase (SEI) layer on the surface of electrode due to the decomposition of electrolyte [34].

Figure 7 shows the cycling performance and rate capability of the MnO$_2$-graphene composite electrode at a current density of 100 mA g$^{-1}$. It can be seen that the MnO$_2$-graphene electrode exhibits good cycling stability, and there is no obvious capacity decay after the first cycle. The coulombic efficiency of the MnO$_2$-graphene electrode was maintained over 95% (except for the first 3 cycles), and this is probably ascribed to the stable sandwich structure of MnO$_2$-graphene composite. The graphene encapsulation enhanced interaction between MnO$_2$ and graphene, and also hindered direct contact between MnO$_2$ and the electrolyte. As the cycling test proceeded, the materials which was wrapped inside become electrochemically active as they come into contact with the electrolyte [35].

To evaluate the rate capability of MnO$_2$-graphene composite electrode, cells were cycled at stepped current densities of 0.1A/g, 0.2A/g, 0.4A/g and 0.8A/g. As shown in Figure 7b, at a current
density of 0.1A/g, the MnO$_2$-graphene electrode exhibited better electrochemical performance in the first 55 cycles. When the current densities ascended to 0.2A/g, 0.4A/g and 0.8A/g, the capacities dropped to 581.7 mAh g$^{-1}$, 410.5 mAh g$^{-1}$ and 304.5 mAh g$^{-1}$, respectively. When the current density was dropped back to 0.1A/g, the capacity could be recovered to 686 mAh g$^{-1}$, demonstrating an excellent electrochemical reversibility of the MnO$_2$-graphene electrode.

![Graph](image)

**Figure 7.** (a) Cycling performance and (b) Rate capability curves of the MnO$_2$-graphene composite electrode at a current density of 100 mA g$^{-1}$

### 4. CONCLUSIONS

A facile approach to synthesized a sandwich-structured MnO$_2$-graphene composite was developed in this study. Characterization methods such as Raman spectroscopy, SEM and TEM were used to demonstrate that MnO$_2$ nanoparticles were well anchored on the surface of graphene and sandwiched between the layers. The electrochemical tests results showed that the MnO$_2$-graphene composite exhibits a high initial capacity of 746 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$, and retained a capacity of 752 mAh g$^{-1}$ after 65 cycles. With the improved electrochemical performance, the nanocomposite could be a promising electrode material for lithium-ion batteries.

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### References


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