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Synthesis and electrochemical performance of mesoporous MnC₂O₄ nanorod/rGO composite anode for lithium-ion batteries

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ABSTRACT:

MnC₂O₄ is a promising anode material for high-energy lithium-ion batteries due to its low cost and high capacity. However, its application is limited by the poor cyclic-stability and rate performance caused by its low conductivity. Herein, mesoporous MnC₂O₄ nanorod/rGO composite is prepared *via* precipitation followed by a reflux reduction process, where MnC₂O₄ nanorods are attached to the surface of graphene through electrostatic adsorption. This composite delivers a discharge capacity of 1082, 964, and 808 mAh·g⁻¹ after 200 cycles at 3, 5, and 8 C, respectively. The good electrochemical performance can be attributed to the synergistic effect between mesoporous nanorods and rGO. This synergistic effect not only offers high conductivity, nanoparticles, and abundant mesopores to accelerate electrode kinetics but also provides a more stable structure to reduce the volume effect during the charge/discharge process. Therefore, mesoporous MnC₂O₄ nanorod/rGO composite can find a potential application in high-energy lithium-ion batteries.

Keywords: Lithium-ion batteries; Anode; Manganese oxalate; Graphene.

1. Introduction

Inspired by the successful application in portable electrical appliances, the application field of lithium-ion batteries (LIBs) has been expanded to large-scale energy storage systems (ESSs) and (hybrid) electric vehicles (EVs) [1-3]. However, performance (e.g. energy/power density, cycle life and safety, etc.) and cost of LIBs in the current state cannot meet the requirements of ESSs, and Evs, which are mainly determined by anode and cathode materials [4]. Graphite is the mainstream anode material for commercial LIBs, but low capacity ($372 \text{ mAh}\cdot\text{g}^{-1}$) and sluggish electrode kinetics limit its application in ESSs, and EVs [4, 5]. Therefore, many efforts have been devoted to developing advanced anode materials instead of Graphite anode [4, 6].

Since Tirado group's pioneer work, transition metal oxalate anode materials have attracted more and more attention due to their high capacity [7–12]. For example, the capacity of CoC_2O_4 ($\sim 900 \text{ mAh}\cdot\text{g}^{-1}$) is more than twice that of graphite [9]. However, the large-scale application of CoC_2O_4 is limited by the cost and toxicity of cobalt. Compared with cobalt oxalate, manganese oxalate is a more suitable anode material for LIBs due to its abundant resources, low toxicity, and small volume change during charge/discharge processes [7, 9]. However, the low conductivity makes the cycle stability and rate performance of manganese oxalate poor [7, 9, 11-13].

Like other conversion reaction-based anode materials [14], designing nanostructured transition metal oxalates with special morphology is an effective approach to improve their performance [11-13]. For example, FeC_2O_4 nanorod gave a capacity of $640 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles at 10 C, exhibiting an enhanced performance [13]. MnC_2O_4 microtubes delivered a high reversible capacity of $925 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles at 1 $\text{Ah}\cdot\text{g}^{-1}$ [15]. On the other hand, compositing with carbon materials is also an important approach to enhance the performance of transition metal oxalates [11-13]. Among the carbon materials studied, graphene has become a promising candidate due to its high conductivity, high surface area, unique flexible structure, and good chemical/thermal stability [16, 17]. Some studies have shown that the cycle stability and rate performance of $\text{Cu}_{1/3}\text{Co}_{2/3}\text{C}_2\text{O}_4\cdot x\text{H}_2\text{O}$ [18], $\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ [19], SnC_2O_4 [20, 21], and FeC_2O_4 [22, 23] can be greatly improved by compositing with graphene. For example, the discharge capacities of $\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O}/\text{rGO}$ was $586 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C, while that of $\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ was only $207 \text{ mAh}\cdot\text{g}^{-1}$ [19]. $\text{SnC}_2\text{O}_4/\text{rGO}$ exhibited a charge capacity of $620 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles at 0.1 C, and the pure SnC_2O_4 only delivered $192 \text{ mAh}\cdot\text{g}^{-1}$ [20]. Therefore, it is expected to further improve the performance of MnC_2O_4 through the combination of nanostructure and graphene sheets. Compared with MnC_2O_4 microtubes [15], this synergistic effect between the nanostructured MnC_2O_4 and graphene sheets possesses two important

advantages: (1) shorten the diffusion distance of Li^+ by nanosized active material; (2) improve the conductivity of MnC_2O_4 by compositing with graphene. However, to the best of our knowledge, there is little report about the nanostructured $\text{MnC}_2\text{O}_4/\text{rGO}$ nanocomposites as the anode of LIBs.

In this work, mesoporous MnC_2O_4 nanorod/rGO composite (MRGO) was prepared *via* precipitation followed by a reflux reduction process. MnC_2O_4 nanorod is anchored onto the surface of rGO nanosheets through electrostatic adsorption. As an anode material for LIBs, MRGO delivers a discharge capacity of $808 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles at 8 C, which is $240 \text{ mAh}\cdot\text{g}^{-1}$ higher than that of bare MnC_2O_4 . The improved performance of the MRGO can be attributed to the synergistic effect of mesoporous MnC_2O_4 nanorods and rGO sheets. This synergistic effect has a series of advantages, including high structural stability, high electron conductivity, and large ion mobility.

2 Experimental

2.1 Materials synthesis

All the reagents are of analytic grade and purchased from Xilong Chemical Reagent Co. Ltd. Graphene oxide (GO) was prepared from graphite powder using a modified Hummers method [24]. 20 mmol $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and 0.23 g GO (8% by mass of manganese oxalate) were dissolved in 75 ml of dimethyl sulfoxide (DMSO) to form a solution A.

20 mmol $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 25 ml of ethylene glycol (EG) to form solution B. Solution B was added into solution A at 5ml/ min. After vigorously stirring for 10 minutes at 40 °C, the precipitate was filtered and washed with water to get hydrated manganese oxalate/GO composite (MHGO). To reduce GO to rGO, After, the MHGO was dispersed in a 120 ml mixture of N-Methyl pyrrolidone (NMP) and water with a volume ratio of 5:1 and refluxed at 170 °C for 1h in air atmosphere [25]. The prepared hydrated manganese oxalate precursor/rGO composite (MHRGO) was dried under vacuum at 150 °C for 3 h to obtain manganese oxalate/rGO composite (MRGO). Bare hydrated manganese oxalate (BMH) and bare MnC_2O_4 (BM) were also obtained as a contrast sample according to the above processes without graphene.

2.2 Materials characterization

A Rigaku D/max-2400 powder X-ray diffractometer was used to collect X-ray diffraction (XRD) data in the 2θ range of 10 and 70°. The shape, size, and crystallinity of samples were observed *via* scanning electron microscopy (SEM; S-3400N) and high-resolution transmission electron microscopy (HRTEM; FEI Tecnai G2 F20). Thermogravimetric analyzer (TGA; SDT-Q600) measurement was performed under nitrogen at a rate of 10°C/min⁻¹ from room temperature to 600°C. The products were also characterized with Fourier-transform infrared (FT-IR; IS50, Thermo Nicolet, USA) spectroscopy. Raman spectroscopy was completed

using a Renishaw inVia Reflex (Renishaw Corporation, London, UK) with a laser of 785 nm wavelength. N₂ adsorption/desorption isotherm experiments were performed on a Micromeritics TriStar II 3020 surface area and porosity analyzer. The specific surface area and the pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

2.3 Electrochemical measurements

CR2032-type coin half-cell was used to evaluate the electrochemical performances of the MRGO and BM. CR2032-type coin cell was assembled in a glovebox in a dry, high-purity argon atmosphere. The used coin cell consists of the working electrode, lithium foil anode, polypropylene porous separator (Celgard 2400), and electrolyte (1 M LiPF₆ + 1% VC/EC-DEC-EMC). To get the working electrode, the active material (MRGO or BM), acetylene black, and Li-PAA binder were thoroughly mixing at a mass ratio of 70:20:10 in water, and the mixed slurry was coated on a copper foil and dried under vacuum at 120 °C overnight. The working electrode was punched and weighed. The galvanostatic charge/discharge tests were conducted on a BTS 4008 battery cycler (Shenzhen NEWARE Electronics Co., Ltd., Shenzhen, China) under different C rates in the range of 0.01-3.0 V (vs. Li/Li⁺) at 25 °C, and 1 C is 375 mA·g⁻¹. The specific capacity and the charge/discharge current were calculated according to the mass of the

active material in the working electrode. An Interface 1010E electrochemical workstation (Gamry Instruments, Warminster, USA) was used to perform cyclic voltammetry (CV) in the range of 0.01–3.0 V and electrochemical impedance spectroscopy (EIS) from 10^5 Hz to 10^{-3} Hz. All electrochemical measurements were performed at 25 °C.

3 Results and discussion

3.1 Structure and morphology characterization

Figure 1.

Figure 1 presents the structural information of the prepared samples obtained by XRD, FT-IR, and Raman. The XRD patterns in Fig. 1(a) are well indexed into monoclinic α -phase $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with a $C2/c$ space group (PDF # 25-0544), indicating the prepared hydrated manganese oxalate in MHRGO and BMH is monoclinic $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [9, 15]. The XRD spectra in Fig. 1(b) are consistent with orthorhombic β -phase MnC_2O_4 with the $Pmna$ space group (PDF # 32-0646) [9, 15], demonstrating the dehydrated manganese oxalate in MRGO and BM is orthorhombic MnC_2O_4 . Monoclinic $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ can be converted to orthorhombic MnC_2O_4 by removing the crystal water [9, 15]. For GO, its XRD pattern usually has a (002) peak at 12.4° [26]. However, no obvious diffraction peak can be observed at 12.4° , suggesting that GO is reduced to rGO [25]. Figure 1(c) compares the FT-IR spectra of MHRGO and BMH. As shown in Fig. 1(c), the peaks at 1361 and 1317 cm^{-1} are related

to the asymmetric and symmetric stretching vibrations of C-O, respectively [27, 28, 29]. The band at 1590 cm^{-1} corresponds to the stretching vibration of the carbonyl group, and the strong peak at 805 cm^{-1} is associated with C-C-O asymmetric vibration [27, 28, 29]. The band at 540 cm^{-1} can be attributed to Mn-O, and the large broad peak at 3385 cm^{-1} means the presence of crystal water [27, 28, 29]. FT-IR analysis indicates that Mn-based precursors in MHRGO and BMH are hydrated manganese oxalate. As depicted in Fig. 1(c), a peak at 1630 cm^{-1} in the MHRGO spectrum can be attributed to the stretching vibration of the C = C bond in the graphite domain of graphene sheet [30, 31], meaning the existence of rGO. Figure 1(d) displays the Raman spectra of MHRGO. As shown in Fig. 1(d), the peak at 1340 cm^{-1} is ascribed to the D band corresponding to the broken edge plane and the defect disordered structure of hexagonal graphite lattice, and the peak at 1590 cm^{-1} is attributed to the G band standing for graphitic structure [17, 19, 21, 25, 26]. The wide and overlapped 2D (2732 cm^{-1}), D+G (2915 cm^{-1}), and 2D' (3146 cm^{-1}) peaks indicate the multilayered structures of the prepared rGO sheets [21, 26]. Higher I_D/I_G (1.65) indicates the increase of defects in graphene after reduction due to the removal of oxygen atoms from the graphene layer [26, 32]. In fact, the removal of oxygen-containing functional groups and the recovery of π - π conjugation during the reduction process are accompanied by the increase of the electronic

conductivity of graphene [32], which is beneficial to improve the electrochemical performance of the MRGO.

Figure 2.

To determining the content of crystallization water and rGO, thermogravimetric analysis was performed to investigate the thermal decomposition process of the MHRGO and BMH. Figure 2 gives the corresponding TG curves. As shown in Fig. 2, the TG curves for BMH and MHRGO have two distinct weight loss stages in the ranges of 100 to 200 °C and 300 to 450 °C, respectively. The first weight loss of BMH (20.3%) is close to the theoretical weight loss of the dehydration reaction of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{MnC}_2\text{O}_4 + 2\text{H}_2\text{O}$, 20.1 wt%) [15]. The second weight loss of BMH (42.5 %) is close to the theoretical weight loss of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposition into MnO ($\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{MnO} + \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$, 40.2 wt%) [15]. The first weight loss of MHRGO (18.3%) is 1.8% less than the theoretical weight loss of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Therefore, the weight percentage of rGO in the MHRGO composite is about 9%, meaning a higher loading density of manganese oxalate on graphene nanosheets.

Figure 3.

A field emission scanning electron microscopy was applied to characterize the morphologies of $\text{MnC}_2\text{O}_4/\text{rGO}$ and MnC_2O_4 . As seen in Fig. 3, graphene has a great influence on the size of the prepared samples.

MnC₂O₄ without rGO is microrod with a length of ~ 10 μm and a diameter of about ~2 μm (Fig. 3(a, b)). MnC₂O₄/rGO composite is an aggregate formed by rod-like nanoparticles. (Fig. 3(c, d)). Therefore, TEM and HRTEM were performed to further clarify the microstructure of rod-like nanoparticles in MnC₂O₄/rGO composite, and the corresponding images are exhibited in Fig. 4. As shown in Fig. 4 (a, b), MnC₂O₄ is a nanorod with a length of 300 – 800 nm and a diameter of 30 – 50 nm, and MnC₂O₄ nanorod attaches to the surface of rGO. A clear interface between MnC₂O₄ nanoparticles and rGO implies the formation of a unique wrapping structure (Fig. 4 (c)). MnC₂O₄ particle has clear lattice fringes with a spacing of 0.36 nm, which can match its (200) crystalline plane (Fig. 4(d)).

Figure 4.

Figure 5.

Figure 5 illustrates the formation process of MnC₂O₄·2H₂O in the presence of graphene. Graphene oxide (GO) prepared by the modified Hummers method contains many oxygen-containing functional groups such as –COOH, –OH, etc. [16, 17]. These oxygen-containing functional groups cannot be dissociated in an aprotic solvent DMSO. On the other hand, MnAc₂·4H₂O dissolves in proton solvent EG to form a solvated manganese ion ($[\text{Mn}(\text{EG})_n]_{\text{sol}}^{2+}$). The addition of EG to DMSO can not only dissociate oxalic acid into C₂O₄²⁻ anion, but also dissociate

oxygen-containing functional groups of GO to make it negatively charged. Therefore, the positively charged $[\text{Mn}(\text{Solvent})_n]_{\text{sol}}^{2+}$ will adhere to the negatively charged oxygen-containing groups of GO through electrostatic attraction. The adsorbed $[\text{Mn}(\text{Solvent})_n]_{\text{sol}}^{2+}$ can act as the nucleation site of manganese oxalate, which makes manganese oxalate grow preferentially on the surface of GO nanosheets. At the same time, the steric hindrance of GO nanosheets can restrict the growth and agglomeration of manganese oxalate, thus resulting in uniform distribution of manganese oxalate nanorods [18, 19, 21]. The flexible structure of GO makes it can warp and coat on the surface of manganese oxalate [22, 26]. After treatment in NMP and dehydration, $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanorod/GO composite can be transformed into mesoporous MnC_2O_4 nanorod/GO composite.

Figure 6.

As shown in Fig. 3, there are cracks and pores in the prepared MRGO and BM. Therefore, N_2 isothermal adsorption/desorption experiments were carried out to investigate the porous structure of MRGO and BM. Figure 6 presents the absorption/desorption curves of MRGO and BM. As given in Fig. 6, all adsorption/desorption curves have an H3-type hysteresis loop at a relative pressure of 0.5–1.0, indicating the mesoporous structure of MRGO and BM [33]. Table 1 lists the surface area, pore size, and pore volume calculated from the absorption/desorption data. As seen in Table

1, MRGO has a larger specific surface area and pore volume than that of BM. These results demonstrate that mesoporous MnC_2O_4 nanorod /GO composite can improve the conductivity, provide more active centers and migration channels for lithium ions, and thus have better electrochemical properties.

Table 1.

In summary, XRD, FT-IR Raman, TG TEM/HRTEM, and N_2 isothermal adsorption/desorption results show that the final products after vacuum dehydration are mesoporous MnC_2O_4 nanorod/rGO composite (MRGO) and mesoporous MnC_2O_4 microrod (BM).

3.2 Electrochemical performance

Figure 7.

The galvanostatic charge/discharge (GCD) technology was used to evaluate the cyclic-stability and the rate performances of the prepared samples. Figure 7 gives GCD curves and cycle performance of MnC_2O_4 nanorod /GO composite (MRGO) and MnC_2O_4 microrod (BM). As given in Fig. 7(a, c), all discharge curves consist of a rapid decline curve from 3.0 to 0.3V, a discharge platform at 0.3V, and a slope below 0.5V [9, 15, 18-22, 27, 28]. The platform at 0.3 V corresponds to the conversion reaction of MnC_2O_4 [9, 15]. The slope below 0.5 V can be ascribed to the pseudo capacitance behavior of the polymeric gel-like layer and the interface lithium storage behavior [9, 11, 34, 35]. The rapid decline curve

from 3.0 to 0.5V is related to the SEI film formation [9, 15, 18-22, 27, 28]. In addition, the initial coulombic efficiency of BM and MRGO is 52 and 46%, respectively. The low initial coulombic efficiency can be attributed to the irreversible crystal-to-amorphous transformation and the formation of SEI film during the first discharge [9, 15, 18-22, 27, 28]. As shown in Fig. 7(b, d), the discharge capacity decreases first and then increases with the increase of the cycles during the initial stage, which is related to the formation and activation of the polymeric gel-like layer [7-12]. The polymeric gel-like layer formed in the first discharge is irreversible and gradually thickened during the initial charge/discharge processes, thus making the discharge capacity decreases first during the initial charge/discharge stage [9, 15, 18-22, 27, 28]. However, this polymeric gel-like layer can be gradually activated and becomes reversible after several cycles [9, 15, 18-22, 27, 28]. Therefore, the discharge capacity increases with after several cycles during the initial stage. As given in Fig. 7(b, d), the capacity of MRGO after 200 cycles at 3, 5, and 8 C is 1082, 964, and 808 mAh·g⁻¹, respectively, while that of BM is only 768, 834, and 570 mAh·g⁻¹, respectively. The above results show that mesoporous MnC₂O₄ nanorod/GO composite has better rate performance and cycle stability.

Figure 8.

The specific capacity in Fig. 7 is higher than the theoretical capacity

of MnC_2O_4 ($375 \text{ mAh}\cdot\text{g}^{-1}$) due to the pseudo capacity from surface reactions [34-27]. To further explore the pseudo-capacitance behavior, CV was performed at different sweep rates. Figure 8(a, b) shows the resulting CV curves. The total current in CV includes the faradaic and capacitive contribution, which can be expressed by the following equation.

$$\begin{aligned} i_{(v)} &= k_1 v + k_2 v^{1/2} \\ \frac{i_{(v)}}{v^{1/2}} &= k_1 v^{1/2} + k_2 \end{aligned} \quad (1)$$

Where $k_1 v$ and $k_2 v^{1/2}$ represent the contribution of capacitive processes and faradaic processes; and k_1 and k_2 can be obtained from the slope and intercept of a linear plot of $i_{(v)}/v^{1/2}$ versus $v^{1/2}$, respectively [15, 28, 37]. Fig. 8 (b, d) displays the capacitive contribution obtained by fitting the CV data with Equation (1). As shown in Fig. 8(b, d), the capacitance contribution of two samples increases with the increase of potential sweep rate, and MRGO has higher capacitance contribution. The higher capacitance contribution of MRGO means better rate performance, which is consistent with Fig. 7(b, d).

Figure 9.

To further explore the effects rGO, EIS was performed to investigate the electrode kinetics of mesoporous MnC_2O_4 nanorod /GO composite and mesoporous MnC_2O_4 microrod. Figure 9 displays the Nyquist plots of MRGO and BM cycled at 3 C. All Nyquist curves consist of a

depressed semicircle at high-to-medium frequencies and a sloped line in the low-frequency region [13, 15, 17, 21, 22, 26, 27]. The depressed semicircle corresponds to the SEI layer resistance and the charge transfer resistance, and the sloped line is related to the Warburg impedance representing the diffusion of Li^+ in the active solid [13, 15, 17, 21, 22, 26, 27]. The equivalent circuit in Fig. 9(a) is used to fit the EIS data, where R_e , R_{SEI} , R_{ct} , Z_W , and C_{dl} are electrolyte resistance, SEI resistance, charge-transfer resistance, Warburg impedance, and capacitive elements, respectively [13, 15, 22]. Table 2 lists the parameters of the equivalent circuit and the diffusion coefficient of Li^+ (D_{Li}) in the active solid. D_{Li} can be calculated by the following equation.

$$D_{\text{Li}} = 0.5 \left(\frac{RT}{n^2 F^2 ACZ_W} \right)^2 \quad (2)$$

Where R , T , n , F , A , and C is gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), absolute temperature (K), charge transfer number ($n=2$), Faraday constant ($96,500 \text{ C} \cdot \text{mol}^{-1}$), the total surface area of the electrode ($1.54 \times 10^{-4} \text{ m}^2$) and the molar concentration of Li^+ in the active materials ($3.37 \times 10^4 \text{ mol} \cdot \text{m}^3$), respectively. As seen in Table 2, the solution resistance (R_s) changes little from the first cycle to the 30th cycle. However, SEI resistance (R_{SEI}) and the charge-transfer resistance (R_{ct}) increase first and then decrease with the increase of cycle, which can be ascribed to the formation and activation of the polymeric gel-like layer during initial charge/discharge process [13, 15, 17, 21, 22, 26]. Compared with that of BM, MRGO has

smaller solution resistance (R_s), SEI resistance (R_{SEI}) and charge-transfer resistance (R_{ct}), and a larger Li^+ ion diffusion coefficient (D_{Li}) due to the synergistic effect between mesoporous nanorods and rGO [18, 21, 28]. This synergistic effect can provide higher conductivity, higher surface area, and more stable diffusion channels, which can accelerate the electrode kinetics and tolerant the volumetric effect in the cycles [18, 19, 22]. Therefore, the cyclic-stability and rate performance of MRGO can be greatly enhanced by this synergistic effect, which further explains the better performance of MRGO in Fig. 7.

Table 2.

4. Conclusions

Mesoporous MnC_2O_4 nanorod/rGO composite was successfully synthesized via precipitation and subsequent reflux reduction process, which utilized electrostatic adsorption between the MnC_2O_4 and graphene sheets. The prepared composite delivers a capacity of 1082, 964, and 808 $mAh \cdot g^{-1}$ after 200 cycles at 3, 5, and 8 C, respectively, exhibiting high capacity, good cyclability and rate performance. The synergy between mesoporous nanorods and rGO not only enhances the electrode kinetics but also alleviates the volume effect during the charge/discharge processes, thereby greatly improving the electrochemical performance of this composite material. The prepared mesoporous MnC_2O_4 nanorod/rGO composite will find potential applications in LIBs.

Acknowledgments

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Tables.

Table 1. Specific surface area, pore size and pore volume of MnC_2O_4 /GO composites and MnC_2O_4

Table 2. EIS Parameters of MnC_2O_4 nanorod/GO composite and MnC_2O_4 microrod.

Figures.

Figure 1. Structural information of the prepared samples: (a) XRD for the hydrated manganese oxalate, (b) XRD for the dehydrated manganese oxalate, (c) FT-IR for the hydrated manganese oxalate, and (d) Raman for the hydrated manganese oxalate/rGO composite.

Figure 2. TG curves of the prepared hydrated manganese oxalate/rGO (MHRGO, black line) and the hydrated manganese oxalate (BMH, red line).

Figure 3. SEM images of (a, b) MnC_2O_4 , and (c, d) $\text{MnC}_2\text{O}_4/\text{rGO}$ composite.

Figure 4. TEM and HRTEM images of $\text{MnC}_2\text{O}_4/\text{rGO}$ composite.

Figure 5. Schematic illustration of the formation of manganese oxalate on the surface of graphene.

Figure 6. N_2 isothermal adsorption/desorption curves of the prepared samples: (a, b) MnC_2O_4 nanorod /GO composites (MRGO), and (c, d) MnC_2O_4 microrods (BM).

Figure 7. Discharge/charge profiles at 5 C and cycle performance at various C rates: (a, b) mesoporous MnC_2O_4 nanorod /GO composite (MRGO) and (c, d) MnC_2O_4 microrod (BM).

Figure 8. CV curves and capacitive contributions to the total capacity of the prepared samples at different sweep rates (v $\text{mV}\cdot\text{s}^{-1}$): (a, b) MnC_2O_4 nanorod/GO composites (MRGO), and (c, d) MnC_2O_4 microrods (BM).

Figure 9. Nyquist plots of the discharged state for different cycles at 3C:
(a) MnC_2O_4 nanorod /GO composite (MRGO) and (b) MnC_2O_4 microrod
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Figures

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Structural information of the prepared samples: (a) XRD for the hydrated manganese oxalate, (b) XRD for the dehydrated manganese oxalate, (c) FT-IR for the hydrated manganese oxalate, and (d) Raman for the hydrated manganese oxalate/rGO composite.

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TEM and HRTEM images of MnC₂O₄/rGO composite.

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Schematic illustration of the formation of manganese oxalate on the surface of graphene.

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Nyquist plots of the discharged state for different cycles at 3C: (a) MnC₂O₄ nanorod /GO composite (MRGO) and (b) MnC₂O₄ microrod (BM).