CuO/rGO nanocomposite as an anode material for high-performance lithium-ion batteries

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Abstract

The porous copper oxide (CuO)/reduced graphene oxide (rGO) composite was prepared by hydrothermal procedure and stirred with graphene oxide dispersion. The composite was employed as anode material to prepare a lithium-ion battery. The effects of different copper sources on the morphology and chemical properties of the materials were studied. Our findings revealed that the structure of CuO with different morphologies was significantly different, which changed the bonding mode of CuO/rGO composites. Our study discovered that the thorn-like B and spherical A and D possess greater capacity and cycle stability. After 100 charge-discharge processes with 200 mAg\(^{-1}\) current density, the reversible capacities were 295 mAhg\(^{-1}\), 290 mAhg\(^{-1}\), and 313 mAhg\(^{-1}\).

1. Introduction

Lithium-ion batteries have played an important part in the customer’s electronic appliances and are still one of the best electrochemical energy storage devices owing to their extraordinary functionalities including their high energy density, long cycle life, environment friendly, and low self-discharge [1]. However, the main limitation in their wide range of applications is that the theoretical capacity of commercial anode material graphite is low. Previously, researchers focused on the alternative anode material to develop lithium ion batteries with better performance, high energy density, rate capability, and cycling stability [2]. In recent years, the transition group metal oxides have fetched much considerations due to its high capacity [3]. In the class of metal oxides, CuO has shown its great potential as a negative electrode material because of its easily availability, cheaper price, stability against chemicals, eco-friendly as well as high theoretical capacity.

To tackle this issue, researchers have developed micro-nano-sized CuO to overcome stress relaxation during lithium extraction [7–9]. Additionally, we tried to add a carbon-based coating material such as graphene to CuO, aiming to alleviate the volume change of CuO during charging and discharging and to increase the contact area between the active material and the electrolyte [10–12]. Due to the mutual attraction of van der Waals forces between graphene layers, it tends to reunite or reorganize into graphite sheets, which requires us to process graphene to increase the wettability and dispersibility of graphene [13–15].

In the current investigation, CuO/rGO composite materials were prepared by a simple and low-cost method. The electrochemical properties of different materials were compared, and the influence of micromorphology on charge-discharge performance was analyzed. Finally, CuO/rGO electrode materials with excellent electrochemical performance were developed.
2. Experimental

2.1. Preparation of CuO/ rGO composite

The 2.5 mmol copper salt and 7.5 mmol urea (AR, 99%) were dissolved in 50 ml distilled water, respectively. The hydrothermal temperature was kept at 160°C for 16 h to obtain four kinds of black copper oxide powders. The copper salts were copper nitrate (AR, 99%), copper chloride (AR, 99%), copper sulfate (AR, 99%) and copper acetate (AR, 98%).

The very next step involved mixing of 25 ml absolute ethanol (≥ 99.5%), 15 ml APTES (BR, 98%), and 10 ml DMF (AR, 99.5%) on the stirrer for half an hour. Graphene (40 mg) (> 99%) was poured into the above solution followed by ultra-sonication for 2 h to achieve stable graphene dispersion.

Further, to obtain the CuO/ rGO composite, four kinds of black powders (400 mg each) were combined with 150 ml absolute ethanol and stirred for 30 min. Then this preparation was added dropwise into the dispersion of graphene oxide under the drainage of a glass rod on the stirrer for 1 h at constant rotating speed to get the final composite of CuO/ rGO. This mixture was then centrifuged with absolute ethanol more than three times until the supernatant was colorless. After centrifugation, the material was placed in a drying oven at 60°C for 12 h. Four kinds of CuO/ rGO composites synthesized by different copper sources were obtained and denoted as: A(Cu(NO3)2-CuO@rGO), B(CuCl2-CuO@rGO), C(CuSO4-CuO@rGO), and D(Cu(CH3COO)2-CuO@rGO).

2.2. Characterization

Through thermogravimetric analysis (TG), x-ray diffraction (XRD), scanning electron microscope (SEM), BET test and electrochemical performance test, four different copper sources of CuO/ rGO composite materials A, B, C and D have been studied. The composition ratio, phase composition, morphology, specific surface area and pore size, and electrochemical performance.

The prepared copper oxide and CuO/ rGO composites were first screened through a 300 mesh sieve and dried in an oven at 120°C for at least 6 h. The binder PVDF with 10% of the total slurry mass was dissolved in a beaker with 40% NMP, and placed in an oven at 120°C until complete dissolution. Then the addition of 80% active material and 10% conductive agent acetylene black was done. An appropriate amount of ball mill rotor, ball mill in a planetary ball mill for about 8 h to obtain a slurry with a medium viscosity and a uniform distribution of the mixture. After mixing, the slurry was evenly coated on the copper foil collector under the guidance of the coating knife surface, followed by the drying process in an oven at 120°C for 30 min, and then rolled into negative electrode plates. A round negative plate with the same size, smooth surface, and no Burr on the edge was made by a punching machine.

The negative plates were selected and weighed, and then placed in the vacuum drying oven at 60°C for one day, together with the diaphragm, positive and negative electrode metal shell, beaker, disposable dropper, and tweezers. Then the button battery assembly work was carried out, and the lithium piece in the glove box was taken as the counter electrode piece. In the glove box with argon protective atmosphere, the negative shell was selected first and then operated in the order of putting lithium plate, adding diaphragm, dropping electrolyte, putting gasket, gasket and covering positive shell. The operation process ensured the wetting and the edge was made by a punching machine.

The negative plates were selected and weighed, and then placed in the vacuum drying oven at 60°C for one day, together with the diaphragm, positive and negative electrode metal shell, beaker, disposable dropper, and tweezers. Then the button battery assembly work was carried out, and the lithium piece in the glove box was taken as the counter electrode piece. In the glove box with argon protective atmosphere, the negative shell was selected first and then operated in the order of putting lithium plate, adding diaphragm, dropping electrolyte, putting gasket, gasket and covering positive shell. The operation process ensured the wetting and flatness of each electrode piece and diaphragm and completed the assembly process of the button battery. The water content and oxygen content of the glove box were kept below 1.0 ppm. The button cell was retained at room temperature for two days to ensure that the electrolyte is completely soaked in the negative electrode material.

The electrochemical properties of the composite were examined by constant current charge-discharge cycle test, rate cycle test, and cyclic voltammetry electrochemical test.

3. Results and discussion

3.1. XRD analysis

Figure 1 (a) exhibits the diffraction pattern of copper oxide in hydrothermal reaction. The results revealed that the products of different copper sources and urea hydrolysis were decomposed into copper oxide, and the powder composition was single, and there was no other impurity phase. The diffraction peak positions in the figure are 13.8°, 16°, 22° and 35° corresponding to (200), (210), (310), and (222) crystal planes, respectively. Compared with figure 1 (b), the diffraction peak of the CuO/ rGO composite is consistent with that of the CuO standard PDF card. Due to the high strength of CuO crystal and the large proportion of composite mass, the diffraction peak of graphene was compressed behind the background peak of the composite. In figure 1 (b), the stronger peaks at the CuO position of CuO/ rGO composites decreased in varying degrees. The findings depicted that the structure of graphene was changed before and after the composite, and the oxygen-containing
functional groups on the surface of graphene hindered the diffusion, crystallization, and growth of copper oxide grains [16].

3.2. TG analysis
The thermal behavior of the CuO/rGO nanocomposite was investigated by using thermogravimetric analysis (TGA). Figure 2 shows the precise affirmation of the weight ratio of the rGO and CuO in the composite. All samples show a uniform trend. The first step of weight loss (about 4%) from 30 °C to 330 °C is attributed to water loss. Approximately from 330 °C to 430 °C, the weight percentage of the material drops sharply until it remains basically constant after 500 °C, because of the decomposition of carbon skeleton from rGO during the oxidation process. The weight reduction of each sample is approximately 9.2%, 8.8%, 9.2%, 9.4%, which is close
to the ratio of the material rGO to CuO 1:10. And the weight kept in about 86%, associating to the content of CuO.

3.3. SEM analysis
Figure 3 shows the scanning electron microscope of CuO with different morphologies prepared by the hydrothermal approach. It can be seen from Fig. (a) and Fig. (b) that the copper nitrate and urea were formed
into spherical copper oxide with a diameter of about 3 μm by solution hydrothermal condensation. Scanning pictures at low magnification demonstrated that the particles have good homogeneity and dispersion, and only a small number of particles were agglomerated. Fig. (d) presents the synthesis of copper oxide by employing copper chloride as the copper source. Its morphology was similar to that of thorn, and the nanoflake clusters were distributed into one particle. It can be seen from diagram (c) that the growth process of hydrothermal reaction grains was not finished, and there was a copper oxide with a large size difference.

The coral-like copper oxide particles with copper sulfate as a copper source can be seen in Fig. (e) and (f). The overall size of copper oxide particles was close to 30 μm. The size of small particles was larger, which may have a great impact on the subsequent electrochemical performance. Fig. (g) and (h) show the morphology of copper oxide with copper acetate as the copper source, with spherical particles of about 3 μm in size. Under the low-power electron microscope, some particles were damaged.

Copper oxide with different morphologies was obtained by different copper salts based on the difference of anions in copper salts. In the process of urea hydrolysis, different morphologies of precipitated grains were formed due to the different anionic affinity in the solution. Copper acetate and copper nitrate had similar anion affinity, and similar spherical particles were formed [17].

The morphology of the composite obtained by hydrothermal treatment is displayed in figure 4. However, figures 4(a)–(h) correspond to the composites with copper sources of copper nitrate, copper chloride, copper sulfate, and copper acetate, respectively. Graphene coated copper oxide particles with different morphologies and sizes, the original morphology of copper oxide was unchanged. A small part of large size copper oxide was decomposed into small particles after bonding, which was consistent with the drop of characteristic peak intensity in the XRD diffraction pattern of CuO/rGO.

3.4. Specific surface area and pore distribution (BET) analysis

The nitrogen adsorption-desorption curve and pore size distribution of the composite are presented in figure 5. The change trend curve in the figure is consistent, and the adsorption hysteresis loop appears in the middle of a bulge after the isotherm, which conforms to the type IV curve, indicating that the composite materials were all mesoporous [18]. During the hydrothermal reaction, the change in thermal decomposition of CuO precursor and the structural morphology of the composite developed the pore structure [19]. According to bet calculation, the specific surface areas of porous composites were 74 m² g⁻¹, 71 m² g⁻¹, 54 m² g⁻¹, and 64 m² g⁻¹, respectively. The small figure in figure 5 is the pore size distribution of the composite, and the pore size of the sample was concentrated in the range of 4 nm.

The pore size of CuO/rGO composites with copper chloride as copper salt was wider than 25 nm indicating the formation of more pore channels due to the combination of thorny copper oxide and graphene. During the process of recharging and discharging, the changes in pore size and channel increased the penetration of electrolyte to electrode materials, increasing specific capacity.

4. Analysis of electrochemical performance

The electrochemical properties of the composites were tested by a button cell. Figure 6 shows the first three cyclic voltammetry curves of (a), (b), (c), and (d) electrode materials. When the electrode material was discharged, the corresponding three reduction peaks correlated to the formation of intermediate phase Cu_x^{2-}O_x, Cu_x^{2+}O_x and the transformation of CuO into copper particles. The oxidation-reduction reaction is as follows.

\[ 2\text{CuO} + 2\text{Li}^{+} + 2e^{-} \rightarrow 2\text{Cu}_{x}^{2-}\text{O}_{x} + \text{Li}_{2}O \]
\[ 2\text{Cu}_{x}^{2-}\text{O}_{x} + 2(1 - x)\text{Li}^{+} + 2(1 - x)e^{-} \rightarrow x\text{Cu}_{2}O + (1 - x)\text{Li}_{2}O \]
\[ \text{Cu}_{2}O + 2\text{Li}^{+} + 2e^{-} \rightarrow 2\text{Cu} + \text{Li}_{2}O \]

As shown in Fig. (c), the three reduction peaks were 0.71 V, 0.95 V, and 2.11 V, respectively. During the subsequent delignification process, the weak anode peak relates to the decomposition of the organic layer and the partial evolution of copper into Cu²⁺ and Cu^{2+}. The decline of the peak type intensity and area of the three-cycle CV Curve correlates with the irreversible capacity loss during the charging and discharging process of CuO, which was due to the incomplete decomposition of the passive film. In figures 6 (a) and (c), during the deintercalation, a small oxidation peak at 2.53 V was observed in the 1st cycle, but it was shifted to about 2.4 V during the 2nd and 3rd cycle. It was the first activation process of the battery. Firstly, when preparing the negative electrode material, some active materials were remained, and the oxidation reaction was occurred during the charging process to generate stable oxides. The discharge process does not participate in the reaction, which leads to a decrease in the potential during the subsequent cycle. Secondly, the deintercalation of lithium ions and
the formation of the electrolyte reacted to form an SEI layer, which established a more stable channel for the deintercalation of lithium ions, resulting in a decrease in the potential in subsequent cycles.

Figure 7 shows the potential versus capacity curve of the composite at 0.2\text{ag}^{-1} current density. Figures (a)–(d) represents composites A, B, C, and D, respectively. The discharge voltage platform was shifted to high voltage, which was a typical characteristic of transition metal oxide electrode materials. In the first cycle, the slope possessed multiple small platforms, which indicated that there was a multiphase transition between CuO and Li. The initial discharge capacities of CuO/rGO composites with different morphologies were 639, 597,
Figure 5. BET curves of CuO/rGO composites with different morphologies.

Figure 6. CV curves of CuO/rGO composites.
433, and 618 mAhg\(^{-1}\), respectively, and the second cycle capacities were 325, 334, 309, and 364 mAhg\(^{-1}\), respectively. The solid electrolyte SEI film formed during the first discharge of cupric oxide was partly decomposed, resulting in the decrease of the capacity of the composite [20]. The plateau trend of sample C at 1.5V \(\sim\) 1.0V expressed that there was no obvious electrochemical process, corresponding to the incomplete conversion from Cu\(^{II}\) Cu\(^{I}\)O\(_{1-x}\)/2 to cuprous oxide. The size of coralline CuO was much larger than that of other morphologies, and it has a cluster structure. The passivation and decomposition of electrode material surface were irreversible during cycling, which greatly affects the attenuation of lithium storage performance. The similar cycle curves of (a), (b) and (d) depicted that the thorny B, spherical A, and D electrode materials maintained the relatively stable electrochemical performance.

The cyclic performance curve of the hydrothermal composite is shown in figure 8. Samples A, B, C, and D correspond to figures (a), (b), (c), and (d), respectively. The cyclic capacity of electrode materials A, B, and D was increased at first and then decreased, indicating that the addition of graphene slowed down the attenuation of volume change during charging and discharging of cupric oxide. The volume change process of CuO in the early stage increased the interface between CuO and graphene. Graphene provides a shorter ion transport channel, which was conducive to the ion exchange between active substances and electrolytes, and the performance of electrode materials was improved to a certain extent [21]. After about 15 cycles, the overall capacity of the material declined slowly. After 100 charges and discharge, the reversible capacities of materials A, B, and D were 295 mAhg\(^{-1}\), 290 mAhg\(^{-1}\), and 313 mAhg\(^{-1}\), respectively, which was related to the morphology and size of CuO/rGO composites.

Coralline C in the cycle curve (c) was the capacity change of the whole attenuation, the special morphology and large particle size allowed the unapparent graphene bonding. The degradation rate of electrochemical properties of the composite was mainly affected by CuO particles, which was not alleviated by the synergistic effect of graphene. The charge discharge capacity of the composite was lower than other materials, and the specific capacity was 212 mAhg\(^{-1}\).

To study the charge-discharge performance of the composites under high current density, the variable rate cycling test was carried out. In figure 9, samples A, B, C, and D correspond to figures (a), (b), (c), and (d), respectively. After five cycles of 0.2 Ag\(^{-1}\), 0.5 Ag\(^{-1}\), 1.0 Ag\(^{-1}\), 2.0 Ag\(^{-1}\), and 3.0 Ag\(^{-1}\), the reversible capacities of samples A, B, C, and D were 345 mAhg\(^{-1}\), 344 mAhg\(^{-1}\), 235 mAhg\(^{-1}\), and 317 mAhg\(^{-1}\). The C capacity loss of
the coral-like CuO/rGO composite was obvious, and other composite materials showed stable rate performance and good capacity stability.
The high-capacity performance of cupric oxide possessed a great potential to be applied in the field of the lithium-ion battery, which further needs to be explored. The main bottleneck of CuO materials lies in the special conversion lithium storage mechanism of transition metal oxides, such as the difference of volume change during the charge-discharge process of electrode materials and the low conductivity of its oxides. It is possible to synthesize CuO/rGO composites with smaller sizes by innovative experimental methods. The composite method of graphene and cupric oxide also needs to be improved, and in-depth study on the interface relationship is needed. It is believed that in the future, researchers will conduct a more thorough analysis of copper oxide electrode materials, realizing the effective control of the composite material process on mesoporous materials, and further improve the lithium storage performance of CuO / rGO composites.

5. Conclusion

In summary, we reported the successful synthesis of porous CuO/rGO nanocomposites. The bonding mode of CuO/rGO composites with pore structure was changed after composite, and the pore size was about 4 nm. Our study revealed that the thorn-like B and spherical A and D have greater capacity and cycle stability. After 100 charge-discharge processes with 200 mAg⁻¹ current density, the reversible capacities were 295 mAhg⁻¹, 290 mAhg⁻¹, and 313 mAhg⁻¹, respectively. The addition of graphene improved the charge discharge stability of the composites, but it was not enough to reverse the decay trend of coral-like CuO. Overall, our study suggested that CuO/ rGO nanocomposite could be an excellent candidate for application in the electrical and other fields.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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