Co₃O₄-graphene nanoflowers as anode for advanced lithium ion batteries with enhanced rate capability

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ABSTRACT

The practical application of Co₃O₄ base anode material is severely limited by its extremely low electrical conductivity and large specific volume changes during lithium ion insertion/extraction. Herein, an effective strategy is being implemented to mitigate the capacity fading of Co₃O₄ at high-rate by embedding Co₃O₄ nanomaterial under the reduced graphene oxide (CGF). The CGF composite has been synthesized through a two-step process, involving a hydrothermal reaction of cobalt nitrate hexahydrate and CTAB in the presence of graphene oxide (GO) and a subsequent calcination. When tested as the anode in lithium ion batteries (LIBs), the CGF composite exhibits an obvious enhancement in electrochemical performance, especially in rate capability. Under current density of 1.0 A g⁻¹, the CGF composite could deliver reversible capacity as high as

1120.8 mAh g⁻¹ after 250 cycles. The superior performance of CGF composite may be ascribed to the unique hybrid microstructure, which can alleviate the stresses caused by volume variations, reduce charge transfer resistance, improve the accessibility of anode to electrolyte and increase the tapping density. The results clearly demonstrate that this unique electrode architecture is ideally suited for LIBs.

Keywords: Co₃O₄-rGO nanoflowers, Graphene, Rate capability, Lithium ion batteries, Anode material

1. Introduction

Lithium-ion batteries (LIBs) are energy storage and conversion devices being widely used in portable electronic devices, such as laptop computers, cell phones, and digital cameras, etc. However, to make them applicable in electric vehicles, plug-in electric vehicles, and integrated grid systems, their energy density and rate capability must be improved appreciably.[1-3] The traditional LIBs use graphite as the anode material due to its high Coulombic efficiency and good cycle performance. Nevertheless, the use of graphite anode in LIBs largely limits the energy density and rate capability.[4, 5] In order to boost both energy density and rate capability of LIBs, tremendous efforts have been devoted to exploring new anode materials.

Up to now, transition metal oxides (TMOs) have attracted a lot of attention due to their high theoretical capacities (600~1200 mAh g⁻¹).[6, 7] Among various TMOs based materials to date, cubic structure Co₃O₄ is a promising anode material due to the high theoretical specific capacity of 890 mAh g⁻¹ based on conversion reaction: $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightleftharpoons 3\text{Co} + 4\text{Li}_2\text{O}$. However, like all other TMOs, Co₃O₄ based anode materials suffer from poor cycling performance and low rate capability owing to their extremely low electrical conductivity and large specific volume changes

during lithium ion insertion/extraction. In order to tackle those challenges, plenty of fundamental studies have been developed in nanostructuring materials, such as nanorods, nanospheres and nanoplatelets, which can relax the strains caused by the volume variations and improve the accessibility of anode to the electrolyte, thus leading to the enhancement of electrochemical performance.[8, 9] Although the improvement of cycling performance and rate capability can be observed through nanostructuring the Co_3O_4 materials, the high performance can not be maintained after long-term cycling due to the collapse of nanostructure. Strategies employed to increase the cycling performance of Co_3O_4 include improving the mechanical strength of Co_3O_4 or hybridizing Co_3O_4 nanoparticles with conducting matrixes to form complex structure, such as hierarchical Co_3O_4 nanostructures,[10] Hollow $\text{Co}_3\text{O}_4/\text{N-C}$ Polyhedron,[11] Porous Co_3O_4 nanofibers/reduced graphene oxide,[12] $\text{Co}_3\text{O}_4/\text{graphene}$ nanocomposite,[13] and so on. Anode based on Co_3O_4 with a conductive coating usually exhibit a greatly enhanced cycling performance. However, the drawbacks of those complex structure can not be overlooked, including low tapping density and undesirable electrode/electrolyte reaction due to the large surface area. A possible solution to those could be to design a hierarchical micro/nanostructure, where the particles are micrometer dimensions but internally consist of nanomaterials. Owing to presenting the exceptional advantages of both nanomaterials and micromaterials, the unique microstructure may provide a fascinating avenue to produce next-generation electrode materials.[14-16]

Herein, we synthesized CGF composite by calcination the hydrothermal product of cobalt nitrate hexahydrate, cetyltrimethyl ammonium bromide and GO. The obtained cobalt oxide nanomaterials are well wrapped by reduced graphene oxide (rGO) due to the strong interaction between electron-rich Co atoms and electrophilic carbon atoms of rGO. [17-19] As an anode

material for LIBs, the CGF composite exhibits durable high-rate performance, even after 250 cycles, it still can deliver reversible capacity of 1120.8 mAh g⁻¹. Several characterization techniques have been used to reveal the reason for this durable high performance. The results show that the enhanced performance of CGF based anode could be attributed to the unique hierarchical structure, which alleviated the stresses caused by volume variations, reduced charge transfer resistance, improved the accessibility of anode to electrolyte and increased the tapping density.

2. Experimental

2.1 Chemicals and reagents

Flake graphite (325 meshes) was obtained from Alfa., potassium permanganate (KMnO₄, ≥ 99.5%), Sodium nitrate (NaNO₃, ≥ 99%), concentrated sulphuric acid (H₂SO₄, 95%), cetyltrimethyl ammonium bromide (CTAB, 99%), hydrochloric acid (HCl, 37%), hydrogen peroxide aqueous solution (H₂O₂, 35%) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%) were purchased from Shanghai Macklin Biochemical Co. Ltd. All the chemicals were used as received without further purification. The deionized (DI) water through Millipore system (Milli-Q[®]) with a resistance of ~18 MΩ cm⁻¹ was used in the reactions.

2.2 Fabrication of the CGF composite

To synthesize the CGF composite, 100 mg of Co(NO₃)₂·6H₂O and 100 mg of GO (which was synthesized from the flake graphite by a modified Hummers method[20, 21]) were added into 60 mL DI water under vigorous stirring. After a homogeneous solution was formed, 20 mL of 0.02 M CTAB aqueous solution was added into the mixture. The resulting solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. After being sealed, it was hydrothermally

treated at 180 °C for 24 hs. When cooled naturally in the oven, the product was subjected to centrifugation and washed with DI water several times to remove the residual reactants. The obtained solid was then calcinated at 500 °C for 2 hs in nitrogen to produce the CGF composite. In order to demonstrate the importance of GO for the morphology of the CGF composite, a similar synthetic procedure in absence of GO solution was performed.

2.3 Characterization

The surface morphologies of the obtained samples were observed under a scanning electron microscope (SEM, JSM-6150, Japan) at an operating voltage of 10.0 kV and a transmission electron microscope (TEM, a JEM-2100F, JPN) at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns of the products are performed on a Bruker D8 Advance powder 600 X-ray diffractometer (Bruker, GER) with Cu K α ($\lambda=1.5418$ Å) as the radiation source. Raman spectra were measured using a confocal LabRAM HR800 spectrometer (Horiba JobinYvon, FR.) with an excitation wavelength of 514 nm from an argon ion laser. X-ray photoelectron spectra of the samples were determined using X-ray photoelectron spectroscopy (XPS) on a VG Escalab 250 spectrometer (Thermo Electron, UK), using an Al K α X-ray source (1486 eV). N₂ adsorption–desorption isotherms were determined by using a Micromeritics ASAP 2020 (Micromeritics, USA). Samples were degassed at 250 °C for 4 hs under vacuum before analysis.

2.4 Electrochemical measurements

Working electrodes were prepared by mixing active material (80 wt.%), acetylene black (10 wt.%), and polyvinylidene fluoride (PVDF) binder (10 wt.%) in N-methyl-2-pyrrolidinone. After the slurries were coated on Cu foils, the mixed materials were dried at 120°C under vacuum for 12 hs to remove the solvent, and then the electrodes were cut into disks. The mass loading of the CGF composite on each disk was ~0.5 mg. The testing cells (CR 2032 coin-type) were

assembled in an argon-filled glovebox (with less than 1 ppm of oxygen and water vapor), using lithium metal as the counter and reference electrode, 1 M LiPF_6 in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (4:3:3 v/v) as the electrolyte and a Celgard 2400 membrane as the separator. Galvanostatic discharge-charge were imposed to the test cells by an Arbin Instrument at cycling rates ranging from 0.1 A g^{-1} to 20.0 A g^{-1} , between 3.0 and 0.01 V (versus Li^+/Li) at ambient temperature. Electrochemical impedance spectra (EIS) were acquired using a Zahner-elektrik IM6 electrochemical workstation with a perturbation voltage of 10 mV in a frequency range of 0.01 Hz to 100 KHz.

3. Result and discussion

The CGF composite was synthesized through a procedure involving the hydrothermal reaction of $\text{Co}(\text{NO}_3)_2$ and CTAB in the presence of GO and subsequent calcination. Fig. 1a shows a typical SEM image of the GO which has a sheet-like structure with wrinkles and ripples due to the highly pliable nature of the graphitic plane. This is consistent with the morphologies of other GOs reported previously.[22, 23] The construct of CGF composite is shown in Fig. 1c, where the flower-like shape could be clearly identified. The close observation exhibits that the CGF composite is composed of a plenty of non-isotropic nanoparticles with a diameter of 25~55 nm and lengths of hundreds of nanometers(Fig. 1d). The existence of bundle-shaped Co_3O_4 can also be evidenced by the morphology of CGF composite after calcination in air (as shown in Fig. S1). Fig. 1b shows the morphology of hydrothermal product of $\text{Co}(\text{NO}_3)_2$ and CTAB in the absence of GO, which has a rod shape with an average diameter of ~70 nm and no other structures can be observed. This indicates that the presence of the GO is vital for the fabrication of CGF composite. The oxygenic groups on the surface of GO might be able to provide the reaction sites

for the cobalt ions in solution, which facilitates the heterogeneous nucleation of Co_3O_4 . The subsequent bundle-shaped growth could be ascribed to the presence of CTAB, which can change the free energies of the various crystallographic surfaces and thus to alter their growth rates, facilitating the formation of bundle-shaped morphology.[24-26] Fig. 1e exhibits a typical TEM image of the CGF composite, where the presence of Co_3O_4 and rGO with a coverage structure can be observed. This unique structure can be further confirmed by the high-resolution TEM (HRTEM), in which the interfacial structure between rGO and the Co_3O_4 particle can be clearly identified. The crystal structure of Co_3O_4 is verified by the lattice fringes in HRTEM image, where the interplanar spacing of 0.28 nm can be clearly visualized, corresponding to the (220) plane of cubic phase Co_3O_4 . This also can be demonstrated by the selected area electron diffraction (SAED) pattern (inset in Fig. 1f).

Fig. 2 shows the XRD patterns of the obtained composites which were scanned at the rate of 3° min^{-1} in the range of $10\sim 80^\circ$. As shown in Fig. 2a and 2b, all the diffraction peaks can be indexed to the cubic phase Co_3O_4 (JCPDS No. 42-1467) with no other phases or impurities detected, suggesting the high crystallinity of Co_3O_4 . In terms of CGF composite, a diffraction hump shows in the range of $22\sim 28^\circ$ could be attributed to the (002) reflection of a graphitic structure, suggesting the existence of rGO. The decrease in the intensity of the diffraction peaks of the CGF composite compared with those of the bare Co_3O_4 nanorods could be attributed to the presence of the rGO, which attenuates the incident and reflection light of the X-ray. The calculated BET specific surface area of the CGF composite is $106.81 \text{ m}^2 \text{ g}^{-1}$, which is significantly higher than that of the bare Co_3O_4 ($53.78 \text{ m}^2 \text{ g}^{-1}$). The high surface area of the CGF composite may facilitate good accessibility of the active material to the electrolyte (as shown in Fig. S2).

The presence of rGO also can be demonstrated by Raman spectrum in Fig. 3a, where the appearance of two prominent peaks is observed, corresponding to the characteristic G (correspond to the E_{2g} phonon of C sp^2 atoms) and D (relate to the mode of the k point phonons of A_{1g} symmetry) bands of the graphitic structure.[27, 28] In addition, the peaks detected at around 189, 458, 510, 601 and 670 cm^{-1} can be assigned to F_{2g} , E_g , F_{2g}^1 , F_{2g}^2 and A_{1g} modes of Co_3O_4 , respectively.[29, 30] It is worth noting that Fig. 3a shows the shift of Raman peaks of the Co_3O_4 to the relatively high wavenumbers compared with those in Fig. 3b, which indicates an improved interaction between Co_3O_4 and rGO with a possible electron transfer from Co_3O_4 to rGO.[31]

XPS was used to determine the chemical composition of the CGF composite. Due to the embedment of Co_3O_4 in rGO, the XPS survey spectrum of the CGF composite in Fig. 4a only shows the Co peaks with low intensities. The assignment of the Co 2p peaks to Co_3O_4 could be demonstrated by two characteristic peaks at 780.2 and 796.3 eV (inset in Fig. 4a), corresponding to the Co $2p_{3/2}$ and Co $2p_{1/2}$ spin orbital peaks of Co_3O_4 , respectively.[32] Fig. 4b shows the spectral deconvolution of C 1s, in which four different components at binding energies of 284.5 eV, 285.3 eV, 286.8 eV, and 289.7 eV can be seen, corresponding to the graphitic carbon, C–O, C–C=O and $\pi-\pi^*$, respectively. These results consistent with the XPS spectra of the hydrothermal reduction products of GO reported previously, suggesting the presence of rGO.[33, 34] All the aforementioned results confirm the successful synthesis of the CGF composite.

To evaluate the electrochemical performance of the CGF composite as an anode for LIBs, the galvanostatic discharge–charge curves at a current density of 1.0 $A\ g^{-1}$ in the voltage range from 0.01 to 3.0 V have been measured. As shown in Fig. 5a, the first discharge curve shows a long voltage plateau at about 1.0 V, which could be attributed to the reduction of Co_3O_4 to Co and the

formation of a solid electrolyte interphase (SEI) film.[35, 36] The first discharging and charging capacities of the CGF composite are 1707.9 and 1206.7 mAh g⁻¹, respectively, resulting an initial Coulombic efficiency of 70.6%. This irretrievable capacity fading is ascribed to the formation of SEI films and the decomposition of the electrolyte, which also can be demonstrated by cyclic voltammograms of the CGF composite shown in Fig. S3a.[37, 38] Owing to these side effects, the discharge and charge capacities of the CGF composite are gradually reduced in the following discharge/charge cycles, as shown in Fig. 5a and 5c. The increment of Coulombic efficiency in the subsequent cycles suggests an improvement in the reversibility of the electrode reactions along with the cycling. This also can be demonstrated by the near unit Coulombic efficiency of the CGF composite based electrode after the initial several discharge/charge cycles shown in Fig. 5c. A relatively steady reversible discharge/charge capacity of about 1200 mAh g⁻¹ is obtained after 10 cycles. Even after 250 cycles the CGF composite still can deliver charge and discharge capacities of 1114.3 mAh g⁻¹ and 1120.8 mAh g⁻¹, respectively. Compared with the capacities of another Co-based anode materials report previously, the stable reversible capacity of the CGF composite is much higher, suggesting the superiority of using the CGF composite as an anode material for LIBs.[39, 40] This is further supported by its significantly high discharge/charge capacities at different cycling rates. As shown in Fig. 5d, the CGF composite can deliver reversible specific capacities of 2079, 1870, 1473, 1201, 866 and 498 mA hg⁻¹ at the current density of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A g⁻¹, respectively. Even at the significantly higher current densities of 10.0 and 20.0 A g⁻¹, it can still deliver reversible specific capacities of 233 and 105 mAh g⁻¹. Notably, the capacities of the CGF could be recovered to 1198 mA h⁻¹ when the current density returns to 1.0 A g⁻¹, indicating the great prospect of using the CGF composite as anode material for LIBs. Indeed, the reversible capacity of CGF composite is much higher

than the theoretical capacity of Co_3O_4 , which might be due to the participation of rGO in lithium ion storage. This could be demonstrated by the improved capacity contribution from the voltage above 0.5 V vs. Li/Li^+ , corresponding to the faradic capacitance of rGO toward the lithium storage.[31]

For in-depth study on the underlying physics of the CGF electrode leading to the high electrochemical performance, the circulation property of the bare Co_3O_4 based LIBs have been evaluated. As shown in Fig. 5b, the initial discharge and charge capacities of the bare Co_3O_4 are about 1850 and 1242 mAh g^{-1} , respectively, approximating to those of the CGF composite. However, due to the self-aggregation of Co_3O_4 nanorods, the bare Co_3O_4 based electrode suffer a dramatic capacity fading in the subsequent discharge/charge cycles which can be observed in Fig. 5e and Fig. S3b, manifesting the excellent electrochemical performance of the CGF composite. After long discharge/charge cycling, the morphologies of the CGF composite and the bare Co_3O_4 were examined. As seen in Fig. 6a, the structure of the CGF composite maintains well owing to the coverage of rGO, which can efficiently suppress the agglomeration of Co_3O_4 nanomaterial and improve the conductivity of the CGF composite electrode. Conversely, no rod-shape structure can be observed in Fig. 6b, indicting the bare Co_3O_4 experienced severe pulverization after discharge-charge cycling, which leads to the poor cycling stability of the bare Co_3O_4 electrode. All the aforementioned demonstrate the great potential of the CGF composite used as an anode material for LIBs with high energy density and high-rate capability.

To gain some insight into the factors that lead to the high performance of the CGF composite, the electrochemical impedance spectra (EIS) of the bare Co_3O_4 and the CGF composite were measured. As shown in Fig. 7a, the EIS spectra consist of a broad semicircle in high frequency regions and an inclined straight line in low frequency regions, which are assigned to the charge

transfer at the electrode/electrolyte interface and the solid state diffusion of the Li^+ ion in the electrodes respectively. Apparently, the diameter of the semicircle at the high frequency region for the CGF composite is much smaller than that for the bare Co_3O_4 . The shrinkage of the semicircles suggests a substantial decrease of charge transfer resistance due to the intimate contact of Co_3O_4 with rGO. Furthermore, EIS spectra show an increase of the slopes of the straight line in low-frequency region, suggesting a improvement of the lithium insertion/extraction kinetics in the CGF anode. The diffusion coefficient of Li^+ can be calculated from the straight line in the low frequency region according to the following two equations:

$$Z_{\text{Re}} = R_s + R_c + \sigma_w \omega^{1/2} \quad (1)$$

$$D = R^2 T^2 / 2 n^4 A^2 F^4 C^2 \sigma_w^2 \quad (2)$$

Where ω is the angular frequency, σ_w is the Warburg factor, R is the gas constant, T is the absolute temperature, n is the number of moles of charge per ion, A is the electrode area, C is the molar concentration of Li^+ ions, and F is the Faraday constant.[22] Base on the equation (1), the σ_w can be obtained from the slope of the line shown in Fig. 7b (R_s and R_c can be extracted by using equivalent circuit shown in the inset of Fig. 7a), which are 144.17 and 38.04 $\Omega \text{ cm}^2 \text{ s}^{-1/2}$, respectively, for the bare Co_3O_4 electrode and the CGF composite electrode. The Li-ion diffusion coefficient D can then be calculated by using the equation (2), the estimated effective diffusion coefficients of lithium ions are 7.46×10^{-16} and $1.73 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, respectively, in the bare Co_3O_4 electrode and the CGF composite electrode, suggesting the unique architecture greatly enhanced lithium ion transport in the CGF composite electrode. Aforementioned data indicate that the incorporation of Co_3O_4 and rGO nanosheets can effectively improve the electrochemical

performance of the CGF composite electrode. This also can be demonstrated by EIS of the bare Co_3O_4 and the CGF composite after 100 cycles (as shown in Fig. S4).

4. Conclusions

In summary, we have successfully designed a novel strategy to synthesize the CGF composite by using a two-step procedure, involving the hydrothermal reaction of cobalt nitrate hexahydrate and CTAB in the presence of GO and a subsequent calcination. The resulting CGF composite is electrochemically active as the anode material for LIBs. Even after 250 cycles, the CGF composite still can deliver reversible specific capacity of $1120.8 \text{ mAh g}^{-1}$ under the current density of 1.0 A g^{-1} . The observed excellent electrochemical performance of the CGF composite electrode is attributed to the unique architecture, which can efficiently suppress the self-agglomeration of Co_3O_4 nanomaterials and decrease charge transfer resistance of the electrode, whereas the Co_3O_4 nanomaterials inhibit the restacking of rGO. Since a close interaction between rGO and Co_3O_4 , the solid-state diffusion of Li ions in the CGF composite is remarkable, which reduces the charge transfer resistance, and improves the accessibility of anode to the lithium ions, leading to a great enhancement of electrochemical performance of the CGF composite electrode. Furthermore, the methodology may also be applicable to the design of other TMOs based electrode for high-power LIBs.

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Figure Captions

Fig. 1. SEM images of (a) the GO, (b) the bare Co_3O_4 , (c) the CGF composite and (d) close observation of the CGF composite. (e) Low- and (f) high-resolution TEM images of the CGF composite. The inset shows SAED patterns of the CGF composite.

Fig. 2. XRD pattern of (a) the CGF composite and (b) the bare Co_3O_4 .

Fig. 3. Raman spectra of (a) the CGF composite, the inset shows the magnification of Raman signals from Co_3O_4 , and (b) the bare Co_3O_4 .

Fig. 4. (a) XPS survey spectrum of the CGF composite. The inset shows the high-resolution Co 2p of the CGF composite. (b) Deconvolution C 1s spectra of the CGF composite.

Fig. 5. Galvanostatic discharge–charge profiles of (a) the CGF composite and (b) the bare Co_3O_4 at 1.0 A g^{-1} for the different cycles, (c) cycle performance and Coulombic efficiency of the CGF composite at a current rate of 1.0 A g^{-1} , (d) rate capability and cycle performance of the CGF composite. The discharge/charge current rates are indicated in the figure, (e) the comparison of cycling performance of the CGF composite with the bare Co_3O_4 at the current density of 1.0 A g^{-1} .

Fig. 6. SEM images of (a) the CGF composite and (b) the bare Co_3O_4 after 100 cycles of the discharge/charge.

Fig. 7. (a) Impedance spectra (Nyquist plots) of LIBs based on the different electrode materials. The dots refer to the experimental data points, while the solid lines correspond to the fitted curves based on an equivalent circuit shown in the inset. (b) Relationship between Z_{Re} and $\omega^{1/2}$ at the low frequency region.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7