Synthesis of Co₃O₄ Nanoparticles Wrapped Within Full Carbon Matrix as an Anode Material for Lithium Ion Batteries

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Abstract A facile polyol-assisted pyro-synthesis method was used to synthesize Co₃O₄ nanoparticles embedded into carbon matrix without using any conventional carbon source. The surface analysis by scanning electron microscopy showed that the Co₃O₄ nanoparticles ($\sim 20 \pm 5$ nm) are tightly enwrapped within the carbon matrix. CHN analysis determined the carbon content was only 0.11% in the final annealed sample. The Co₃O₄@carbon exhibited high capacities and excellent cycling performance as an anode at various current rates (such as 914.4 and 515.5 mAh g⁻¹ at 0.25 and 1.0 C, respectively, after 50 cycles; 318.2 mAh g⁻¹ at a high current rate of 5.0 C after 25 cycles). This superior electrochemical performance of the electrode can be attributed to the various aspects, such as, (1) the existence of carbon matrix, which acts as a flexible buffer to accommodate the volume changes during Li⁺ ion insertion/deinsertion and facilitates the fast Li⁺ and electron transfer and (2) the anchoring of Co₃O₄ nanoparticles within the carbon matrix prevents particles agglomeration.

KEY WORDS: Co₃O₄; Carbon matrix; Pyro-synthesis; Anode; Lithium ion battery

1 Introduction

Over the past several years, transition metal oxides have been extensively investigated as possible anode materials for lithium ion batteries due to their high theoretical capacities (500–1200 mAh g⁻¹) [1]. Among various metal oxides, Co₃O₄ has been given special attention owing to its most stable performances with excellent reversibility and high theoretical capacity (890 mAh g⁻¹), which is almost more than two times of the graphite anode (372 mAh g⁻¹) [1–8]. However, there are still some factors, which limit the application of Co₃O₄ as a suitable anode material for

lithium ion battery, such as large volume expansion/contraction and severe particle aggregation during Li⁺ ion insertion/deinsertion process, resulting electrode pulverization, loss of particle contacts and rapid capacity fading. Therefore, two popular attempts have been significantly explored to avoid these limitations and improve the electrochemical performances of Co₃O₄ electrode material, such as various morphology design and conductive composite design. It is believed that the nanomaterials design/fabrication can provide short ion/electron transfer path, large specific surface area, additional active reaction sites and longer cycle life, whereas the conductive matrix could improve the electronic conductivity and alleviate the severe volume expansion/contraction during cycling [9, 10]. The synergistic effect between nanoparticles and conductive matrix has been shown to boost the electrochemical performance of Co₃O₄ electrode. However, a uniform dispersion of nanoparticles within a carbon matrix under a facile synthesis process is still a difficult task. Hence, it would not be easy to simultaneously maintain a

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large reversible capacity along with long cycling life, and a good rate capability in nanostructured Co_3O_4 electrode. The intimate correlation between nanomaterials synthesis and their material properties always demands the introduction of new strategies to develop promising nanomaterials to achieve superior properties.

Therefore, we reported here a rapid polyol-based pyro-synthesis method, performed under open-air conditions, to produce carbon-wrapped Co_3O_4 nanoparticles. This process provides an opportunity to uniformly coat all the nanoparticles through a carbon layer without using any external carbon source. The Co_3O_4 has never been synthesized before by pyro-synthesis method to see whether Co_3O_4 nanoparticles could be efficiently distributed within a full carbon matrix, and what would be the electrochemical performance of such a unique nanocomposite electrode. More importantly, the primary fuel is polyol solvent in this pyro-synthesis method, which instantly provides ultrahigh exothermic energy to the surroundings during the combustion. Under the polyol-rich condition, a part of the polyol carbonized to form carbon matrix, whereas most of the part undergo combustion to supply the energy for nucleation of nanoparticles [11]. The entire process was completed within few minutes, which suppresses particle growth and improves the interparticle connectivity. The obtained architecture of Co_3O_4 nanoparticles wrapped within a full carbon matrix exhibits high reversible capacity and excellent cyclic performance. It is believed that the obtained architecture maintains morphological stability and sufficient conductivity of the electrode material.

2 Experimental

2.1 Materials Synthesis

Co_3O_4 nanoparticle within full carbon matrix was synthesized using polyol-assisted pyro-synthesis method. In order to clearly explain the synthesis method, a schematic diagram can be clearly seen in Fig. 1. Cobalt (II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Sigma-Aldrich. Rests of the chemicals used in the experiments

were of analytical grade without further purification. Typically, 0.01 mol of cobalt acetate was dissolved in 80 mL of diethylene glycol ($\text{C}_4\text{H}_{10}\text{O}_3$, 99% Spectrochem) and stirred for 24 h at room temperature. Noticeably, diethylene glycol here acts not only as a solvent and reducing agent but also a carbon source. Afterward, a liquid thinner was added with continuous stirring to the homogenous solution for flammability. An electric torch was used to ignite the solution to induce a self-extinguishable combustion process. A black color powder was directly collected after the combustion process. In order to increase the crystallinity and avoid the reduction of Co_3O_4 , the obtained sample was annealed at 400 °C for 5 h under air atmosphere.

2.2 Materials Characterization

The composition and phase of the products were characterized by Shimadzu X-ray diffractometer ($\lambda = 1.5406 \text{ \AA}$). The surface morphology and particles size of the obtained products were analyzed by field-emission scanning electron microscopy (FE-SEM; S-4800 Hitachi) and field-emission transmission electron microscopy (FE-TEM; FEI 20 FEG). Before drop casting onto copper grids for FE-TEM examination, the samples were dispersed by ultrasonic vibration using ethanol solution. CHN element analysis (Elementar Vario EL III) was used to determine the carbon content in the annealed sample. X-ray photoelectron spectroscopy (XPS) measurement was also performed using Kratos Analytical, Ultra axis with a monochromatic AlK_{α} X-ray source. Raman spectroscopy (WITec Alpha 300 RA) was also used to investigate the existence of both carbon and Co_3O_4 in the sample with a diode laser as the excitation source.

2.3 Electrochemical Testing

In order to measure the electrochemical performance, the electrode was fabricated by mixing the active materials (70 wt%), conductive carbon black (20 wt%), and polyvinylidene fluoride (10 wt%) and casted onto the copper foil by using the doctor-blade technique. Subsequently the hot stainless steel twin roller was used to

Fig. 1 Schematic illustration of the preparation of Co_3O_4 nanoparticles under carbon matrix

uniformly press the slurry in order to improve the adhesion between the Cu foil and active materials. Lithium foil was used as a counter electrode. The electrolyte used was 1 M LiPF_6 in a 1:1 weight ratio of ethylene carbonate and dimethyl carbonate solvent. A glass fiber along with Celgard 2400 membrane was used as the separator. The galvanostatic charge–discharge tests were carried out using an Arbin Battery Tester (BT 2000) in the voltage range of 0.01–3.0 V. The cyclic voltammetry (CV) test was conducted using an Autolab potentiostat (PGSTAT 302 N) with the scan rate of 0.1 mV s^{-1} within the range of 0–3.0 V.

3 Results and Discussion

3.1 Structural and Morphological Analysis

The phase purity and crystal structure of the annealed sample were checked by X-ray diffraction (XRD). Figure 2 shows the XRD pattern of $\text{Co}_3\text{O}_4@\text{C}$ sample after annealing at 400°C for 5 h. All the sharp reflection peaks can be indexed to a standard cubic Co_3O_4 phase (JCPDS Card No. 78-1970), indicating the formation of pure crystalline cubic Co_3O_4 phase.

The surface morphology of annealed $\text{Co}_3\text{O}_4@\text{C}$ sample was investigated by FE-SEM and FE-TEM analysis. From FE-SEM image of Fig. 3a, it can be seen that the primary Co_3O_4 nanoparticles possess an almost spherical shape with a diameter of $20 \pm 5 \text{ nm}$. Furthermore, the primary Co_3O_4 nanoparticles are aggregated into secondary particles, which may be due to their extremely small dimensions and high surface energy. In order to clearly investigate the morphology and distribution of Co_3O_4 nanoparticles in the carbon matrix, the $\text{Co}_3\text{O}_4@\text{C}$ sample

was characterized by FE-TEM. Figure 3b, c, d shows the FE-TEM images of different regions of $\text{Co}_3\text{O}_4@\text{C}$ sample obtained at different magnifications. The clear contrast between the edge and the center confirms the existence of carbon matrix. It is shown that the Co_3O_4 nanoparticles are covered with homogenous carbon frameworks. A typical carbon coating layer can be clearly seen in the magnified inset image of Fig. 3b, d for more clarity, which continuously wraps Co_3O_4 nanoparticles. It is reasonable to suggest that such continuous carbon layers may not only effectively improve the structural stability and conductivity of Co_3O_4 nanoparticles during lithium ion storage, but also act as a buffer to accommodate the volume expansion/contraction during lithium ion insertion/deinsertion. More importantly, the high magnified FE-TEM images in Fig. 3c, d show that Co_3O_4 nanoparticles are fully wrapped within the carbon matrix rather than exposed to the outer surface, which indicates the strong interaction between the nanoparticles and the carbon matrix. In addition, the high magnified image of Fig. 3d reveals a carbon layer of thickness ~ 3 to 4 nm on the particle boundaries of the present sample.

In order to find out the accurate percentage of carbon in the annealed sample, CHN analysis is also performed. CHN analysis of the annealed $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite indicates that the amount of carbon is only 0.11%, which would account for a carbon matrix in the sample, as observed in FE-TEM images of Fig. 3.

XPS was also carried out to further confirm the carbon coating and chemical composition details of the $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite sample. Figure 4 shows the XPS spectra of the annealed $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite sample. The strong peak at 284.6 eV in Fig. 4a is characteristic peak of C-1s, which can be related to the carbon coating in the sample. As shown in Fig. 4b, the XPS spectrum of Co-2p exhibits two peaks located at 780.1 eV (Co $2p_{3/2}$) and 795.2 eV (Co $2p_{1/2}$) with a spin orbit coupling of 15.1 eV , which are typically in good agreement with that of Co_3O_4 phase reported in the literature [12]. The presence of Co_3O_4 can be further confirmed by the O-1s peak at 530.2 eV in Fig. 4c, which can be perfectly assigned to the oxygen species from the Co_3O_4 crystal lattice [12]. Thus, it is reasonable to suggest that the Co_3O_4 nanoparticles are successfully coated by the carbon coating using current pyro-synthesis method. Raman spectrum of the $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite sample was also investigated to demonstrate the existence of both Co_3O_4 and carbon in the nanocomposite sample, as shown in Fig. 4d. Since the amount of carbon is very less in the sample (as determined by CHN analysis), it is believed that the instrument could not identify the D band and G band of carbon in the sample. On the other hand, the peaks of Raman shift at 204.32 , 490.04 , 530.66 , 624.76 and 694.72 cm^{-1} can be

Fig. 2 XRD pattern of annealed $\text{Co}_3\text{O}_4@\text{C}$ sample

Fig. 3 a FE-SEM, b–d FE-TEM images of $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite, respectively

Fig. 4 XPS spectrum of $\text{Co}_3\text{O}_4@\text{C}$ sample a C-1s, b Co-2p, c O-1s, d Raman spectra of the $\text{Co}_3\text{O}_4@\text{C}$ sample

ascribed to the F_{2g} , E_g and A_{1g} vibration modes of Co_3O_4 , which are already reported in the literature [13]. The obtained typical Raman peaks in the spectrum clearly confirmed the presence of Co_3O_4 in the nanocomposite sample.

3.2 Electrochemical Properties

Cyclic voltammetry experiment was initially conducted to evaluate the electrochemical performance of the $\text{Co}_3\text{O}_4@\text{C}$ electrode at a scanning rate of 0.1 mV s^{-1} over the voltage range from 0 to 3.0 V. Figure 5a shows the first five cyclic voltammogram curves of $\text{Co}_3\text{O}_4@\text{C}$ electrode. An irreversible cathodic peak appeared at 0.86 V in the first cycle and shifted to 1.1 V during the subsequent cathodic cycles, which can be attributed to the reduction of Co_3O_4 into Co and Li_2O along with the irreversible formation of an SEI (solid electrolyte interphase) layer ($\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \leftrightarrow 3\text{Co} + 4\text{Li}_2\text{O}$) [14]. In the anodic scan, one peak at 2.1 V is recorded, which is ascribed to the reversible oxidation of metal Co to Co_3O_4 . It can be clearly seen that the CV pattern of the second cycle is almost coincided with the following cycles, indicating that the redox reaction is reversible.

Figure 5b shows the first, second and fifth charge/discharge voltage profiles of $\text{Co}_3\text{O}_4@\text{C}$ electrode at a constant current rate of 0.25 C ($1 \text{ C} = 890 \text{ mA g}^{-1}$). The first discharge curve shows a short voltage plateau at 1.11 V and a long one at 1.05 V followed by a gradual slope to the cutoff potential of 0.01 V, which can be ascribed to the successive reduction of Co_3O_4 to CoO and then to Co along with the formation of SEI layer on the surface of Co_3O_4 nanoparticles [15, 16]. A broad oxidation peak between 2.0 to 2.5 V can be also seen in the charge curves, indicating the reversible oxidation reaction of Co to Co_3O_4 . However, the discharge and charge potential plateaus of the electrode in the subsequent cycles shifted to the higher potential, which is consistent with the CV results. The annealed $\text{Co}_3\text{O}_4@\text{C}$ electrode displays the first discharge and charge capacity of 1103.1 and 847.4 mAh g^{-1} , respectively. The initial Coulombic efficiency is low ($\sim 77\%$), which is due to the irreversible conversion reaction and the formation of the SEI layer on the electrode surface. However, it retains a high reversible discharge/charge capacity of 867.2 and 845.6 and 883.7 and 864.4 mAh g^{-1} in the subsequent second and fifth cycles, respectively. The Coulombic efficiency rapidly rises from 77% in the first cycle to 98% in

Fig. 5 Electrochemical performance of $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite electrode: **a** Cyclic voltammogram curves at a scan rate of 0.1 mV s^{-1} ; **b** discharge/charge voltage profiles at the constant current rate of 0.25 C; **c** comparison of the cyclability at the constant current rates of 0.25 and 1.0 C; **d** C-rate capability at various current rates between 0.5 and 5.0 C

Table 1 Comparison of specific capacities of the current $\text{Co}_3\text{O}_4@\text{C}$ electrode with previous Co_3O_4 electrodes reported in the literature

Materials	Synthesis method	Current density/rate	Cycle number	Specific capacity (mAh g^{-1})	Refs.
Co_3O_4 -C Core-shell nanowire	Hydrothermal synthesis	2.0 C	20	676	[17]
Carbon@ Co_3O_4 nanostructure	Hydrothermal approach	0.5 C	107	567	[18]
–	–	2.0 C	80	423	[18]
Hierarchically porous carbon (HPC)/ Co_3O_4 nanocomposite	Murdannia simplex stalks	1 A g^{-1} (1.1 C)	40	375	[20]
Co_3O_4 /carbon nanotube hybrid	Mechanical Treatment processes	0.2 C	70	877	[21]
Co_3O_4 -carbon nanotube composite	Thermal decomposition	200 mA g^{-1} (0.22 C)	100	776	[22]
–	–	1 A g^{-1} (1.1 C)	35	600	[22]
Co_3O_4 /onion-like carbon nanocomposite	Solvothermal method	200 mA g^{-1} (0.22 C)	100	632	[23]
–	–	2000 mA g^{-1} (2.2 C)	50	154	[23]
Co_3O_4 nanocages	Thermal decomposition	2000 mA g^{-1} (2.2 C)	25	252	[24]
Co_3O_4 /ordered mesoporous carbon nanocomposite	Solvent evaporation-induced co-self-assembly	1.5 A g^{-1} (1.7 C)	35	580	[25]
$\text{Co}_3\text{O}_4@\text{C}$	Pyro-synthesis	0.25 C	50	914.4	*
–	Pyro-synthesis	1.0 C	50	515.5	*
–	Pyro-synthesis	5.0 C	35	318.2	*

* Current study

the fifth one and then remains same in the following cycles (Fig. 5c). It is remarkable to note that the obtained reversible capacity is too close to the theoretical capacity of bulk Co_3O_4 anode (890 mAh g^{-1}). It is believed that the improved capacity is due to the existence of the carbon matrix, which suppresses the side reactions between the active materials and electrolyte, stabilizes the SEI film and increases the kinetics of the conversion reactions [17]. In addition, the small size of the primary nanoparticles in the sample can also provide a short pathway for Li^+ ion diffusion.

The highly improved cycling performance is another excellent advantage of the pyro-synthesized $\text{Co}_3\text{O}_4@\text{C}$ electrode. The capacity versus cycle number curves at two different current rates of 0.25 and 1.0 C for 50 cycles are shown in Fig. 5c. It is apparent that the electrode exhibits stable cycling performance at both the current rates up to the 50th cycle. It can be observed that the $\text{Co}_3\text{O}_4@\text{C}$ electrode at 0.25 C released an initial capacity of 847.4 mAh g^{-1} and maintained a high reversible capacity of 914.4 mAh g^{-1} after 50 cycles, which shows a 100% of capacity retention. In contrast, when applying a high current rate of 1.0 C, the reversible charge capacity was measured to be 791.5 mAh g^{-1} in the first cycle and remained at 515.5 mAh g^{-1} after 50 cycles. It can be seen that the $\text{Co}_3\text{O}_4@\text{C}$ electrode not only delivers more than two times higher reversible capacity than that of graphite anode (372 mAh g^{-1}), but also exhibits an excellent and stable cycle performance after the second cycle. It is

believed that the obtained excellent capacity retention of $\text{Co}_3\text{O}_4@\text{C}$ electrode is due to the unique synergistic behavior between the active material and carbon matrix, particularly the robustness of the carbon layer, which not only acts as a flexible buffer to accommodate the volume changes during Li^+ ion insertion/deinsertion, but also increases the conductivity of the electrode [18].

Since rate capability is an important parameter for batteries applications, the C-rate test was also performed for the $\text{Co}_3\text{O}_4@\text{C}$ electrode at various high current rates between 0.5 and 5.0 C, and the result is displayed in Fig. 5d. It can be observed that the charge capacity step-wise decreases with increasing current rates. As an example, the reversible charge capacities of the $\text{Co}_3\text{O}_4@\text{C}$ electrode at current rates of 0.5, 1.0, 2.0, 4.0 and 5.0 C are 863.6, 798.7, 675.3, 493.5 and 318.2 mAh g^{-1} , respectively. Moreover, when the current rate returns to the initial value of 0.5 C, the $\text{Co}_3\text{O}_4@\text{C}$ electrode still recovers its original capacity (870.1 mAh g^{-1}) after 40 cycles, indicating good reversibility and stability of the electrode material. It is highly probable that the carbon matrix existed in the sample plays an important role to increase the conductivity, decreases the ohmic loss and further offers more sites to accommodate Li^+ ions [19]. It should be especially noted that CHN analysis of annealed $\text{Co}_3\text{O}_4@\text{C}$ sample determined to have only 0.11% of carbon. This small amount of carbon appears to be sufficient for the formation of a carbon matrix as well as boosting the electrochemical performances of the $\text{Co}_3\text{O}_4@\text{C}$ electrode.

In order to clearly evaluate the performance of pyro-synthesized $\text{Co}_3\text{O}_4/\text{C}$ electrode, a comparison between the current study and the previous $\text{Co}_3\text{O}_4/\text{Carbon}$ studies based on different synthesis methods with various microstructures is shown in Table 1 [17, 18, 20–25]. It can be clearly seen that the obtained capacity of the current $\text{Co}_3\text{O}_4/\text{C}$ electrode is comparable than those reported in the literature but the approach to synthesize $\text{Co}_3\text{O}_4/\text{C}$ nanocomposite by the use of novel pyro-synthesis method in the present study is very cost-effective and simple compared to the reported reports.

4 Conclusion

In summary, the Co_3O_4 nanoparticles embedded into conductive carbon matrix were successfully synthesized using the facile polyol-assisted pyro-synthesis method. The XRD pattern confirms the purity of the sample after annealing at 400 °C for 5 h under air atmosphere. The primary particle size is in the range of $\sim 20 \pm 5$ nm. When evaluated as the anode material for LIBs applications, the obtained $\text{Co}_3\text{O}_4/\text{C}$ electrode exhibits large reversible capacity (914.4 mAh g^{-1} at 0.25 C after 50 cycles) with nearly 100% capacity retention, stable cycle life (515.5 mAh g^{-1} at 1.0 C after 50 cycles) and high rate capability (318.2 mAh g^{-1} at 5.0 C after 25 cycles). It can be suggested that the unique architecture and synergistic effect between carbon matrix and Co_3O_4 nanoparticles might contribute to the high electrochemical performance of the $\text{Co}_3\text{O}_4/\text{C}$ electrode. In addition, it is also believed that the high flexibility of the carbon matrix can accommodate the volume changes of the conversion reaction-based electrodes. The current synthesis method opted here is a facile and scalable and could be extended to the other metal oxide anode materials for lithium ion battery application.

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